TECHNOLOGY DEPT.

PUBLIC LIBRARY
FEB 12 1943
DETROIT

JOURNAL OF THE CHEMICAL SOCIETY

DECEMBER, 1942

PATRON:
HIS MAJESTY THE KING

President:
W. H. MILLS, M.A., Sc.D., F.R.S.

Vice-Presidents
who have filled the office of President:

F. G. DONNAN, C.B.E., D.Sc., LL.D., F.R.S.
PERCY F. FRANKLAND, C.B.E., D.Sc., LL.D., F.R.S.
SIR ROBERT ROBINSON, M.A., D.Sc., LL.D., F.R.S.
N. V. SIDGWICK, C.B.E., D.Sc., LL.D., F.R.S.
W. P. WYNNE, D.Sc., M.A., F.R.S.

Vice-Presidents:

F. H. CARR, C.B.E., D.Sc., F.I.C.
A. FINDLAY, M.A., D.Sc., Ph.D., F.I.C.
C. S. GIBSON, O.B.E., M.A., Sc.D., F.R.S.
W. N. HAWORTH, D.Sc., Ph.D., F.R.S.
C. N. HINSHELWOOD, M.A., Sc.D., F.R.S.
J. L. SIMONSEN, D.Sc., F.R.S.

Treasurer:
F. P. DUNN, B.Sc., F.I.C.

Secretaries:

C. W. DAVIES, D.Sc., F.I.C.
G. M. BENNETT, M.A., Sc.D., Ph.D., F.I.C.
W. WARDLAW, D.Sc., F.I.C.

Ordinary Members of Council:

J. W. BAKER, D.Sc., Ph.D., F.I.C.
J. W. COOK, D.Sc., Ph.D., F.R.S.
H. J. T. ELLINGHAM, B.Sc., Ph.D., F.I.C.
H. J. EMELÉUS, D.Sc., A.R.C.S.
F. FAIRBROTHER, D.Sc.
J. J. FOX, C.B., O.B.E., D.Sc., F.I.C.
J. M. GULLAND, M.A., D.Sc., Ph.D.
G. S. HARTLEY, D.Sc.
R. D. HAWORTH, D.Sc., Ph.D., F.I.C.
T. P. HILDITCH, D.Sc., F.R.S., F.I.C.
D. J. G. IVES, Ph.D., A.I.C.
F. B. KIPPING, M.A., Ph.D.
F. G. MANN, Sc.D., D.Sc., F.I.C.
E. B. MAXTED, D.Sc., Ph.D., F.I.C.
S. G. P. PLANT, M.A., D.Phil.
E. H. RODD, D.Sc., A.C.G.I., F.I.C.
J. D. M. ROSS, M.B.E., M.A., D.Sc.
B. C. SAUNDERS, M.A., B.Sc., Ph.D.
H. W. THOMPSON, M.A., B.Sc., Ph.D.
H. B. WATSON, D.Sc., Ph.D., F.I.C.
G. S. WHITBY, D.Sc., Ph.D., LL.D.

Ex-Officio Members of Council:

T. A. HENRY, D.Sc. (*Chairman of the Joint Library Committee*).
L. H. LAMPITT, D.Sc., F.I.C. (*Chairman of the Chemical Council and of the Bureau of Chemical and Physiological Abstracts*).
T. S. MOORE, M.A., B.Sc. (*Chairman of the Publication Committee*).

General Secretary:
S. E. CARR, F.C.I.S.

Acting Librarian:
A. E. CUMMINS.

Telephone Numbers: Office, Regent 6322; Library, Regent 1342

London: THE CHEMICAL SOCIETY, BURLINGTON HOUSE, W.1

Committee of Publication

Chairman: T. S. MOORE, M.A., B.Sc.

A. J. ALLMAND, M.C., D.Sc., F.R.S.
W. BAKER, M.A., D.Sc.
R. P. BELL, M.A., B.Sc.
G. M. BENNETT, M.A., Sc.D.
E. J. BOWEN, M.A., F.R.S.
H. V. A. BRISCOE, D.Sc., F.I.C.
F. CHALLENGER, D.Sc., Ph.D.
J. E. COATES, O.B.E., D.Sc., F.I.C.
J. W. COOK, D.Sc., F.R.S.
C. W. DAVIES, D.Sc., F.I.C.
F. P. DUNN, B.Sc., F.I.C.
W. E. GARNER, D.Sc., F.R.S.
J. M. GULLAND, M.A., D.Sc., Ph.D.
C. R. HARINGTON, M.A., Ph.D., F.R.S.
G. S. HARTLEY, D.Sc.
R. D. HAWORTH, D.Sc., Ph.D.
I. M. HEILBRON, D.S.O., D.Sc., F.R.S.
T. A. HENRY, D.Sc.
D. H. HEY, Ph.D., D.Sc., F.I.C.
E. L. HIRST, M.A., D.Sc., F.R.S.
E. D. HUGHES, D.Sc., Ph.D., F.I.C.
J. KENYON, D.Sc., F.R.S.
F. G. MANN, D.Sc., F.I.C.
H. W. MELVILLE, Ph.D., D.Sc., F.R.S.
W. H. MILLS, M.A., Sc.D., F.R.S.
J. R. PARTINGTON, M.B.E., D.Sc.
A. ROBERTSON, M.A., Ph.D., F.R.S.
S. SUGDEN, D.Sc., F.R.S.
H. TERREY, B.Sc.
A. R. TODD, D.Sc., D.Phil., F.R.S.
W. WARDLAW, D.Sc., F.I.C.

Editor:
CLARENCE SMITH, D.Sc.

Assistant Editor:
A. D. MITCHELL, D.Sc.

Indexer:
MARGARET LE PLA, B.Sc.

Subscription Rate, £3.10.0 per annum, post free

The Chemical Society was founded in 1841 and received a Royal Charter in 1848.

The main function of the Society is to foster original research in Chemistry and to facilitate the discussion and dissemination of new knowledge in all branches of the science.

FELLOWSHIP

Fellowship of the Chemical Society is open to men and women of all nationalities who are interested in Chemistry and wish to keep in touch with its advances. Fellows are elected by the Council.

PRIVILEGES

Fellows who pay the annual subscription of £3 have the following privileges

1. To receive any two of the following publications of the Society without extra charge:

(*a*) *Journal of the Chemical Society.*
(*b*) Reprints of Lectures, etc., published in the *Journal.*
(*c*) *British Chemical and Physiological Abstracts A:* AI, General, Physical and Inorganic Chemistry; AII, Organic Chemistry; AIII, Physiology and Biochemistry, including Anatomy.
(*d*) *Annual Reports on the Progress of Chemistry.*

except that Fellows who choose (a) *and* (c) are entitled to receive *any two* sections only of Abstracts A with Index. If the third section of Abstracts A is also required, it may be obtained at the special price of 19/6. Fellows who do not choose to receive the Annual Reports or Reprints of Lectures free of charge may obtain these on payment of 5/6 each, post free.

2. To consult and borrow the books in the Library (44,000 volumes).
3. To attend meetings of the Society both in London and outside London, and to introduce two guests thereto.
4. To apply for research grants.
5. To submit original papers for publication in the *Journal.*

As a special concession to younger chemists, Fellows who are under the age of 25 have the option of paying half the annual subscription (£1 10s.) and receiving until the end of the year in which they reach that age:

The *Annual Reports on the Progress of Chemistry*, and either the *Journal of the Chemical Society* or two sections of *British Chemical and Physiological Abstracts A.*

Such Fellows receive no other publications of the Society, but enjoy all the other privileges accorded to those paying the full annual subscription.

PUBLICATIONS

(*a*) *The Journal of the Chemical Society*, which is published monthly, contains the results of investigation which cover the whole field of pure chemistry.

(*b*) *British Chemical and Physiological Abstracts.*

The Society collaborates with the Society of Chemical Industry, the Physiological Society, and the Biochemical Society in maintaining the Bureau of Chemical and Physiological Abstracts, which issues every month abstracts of papers dealing with all branches of pure and applied chemistry and physiology published in all parts of the world.

British Chemical and Physiological Abstracts A is divided into three sections: AI, General, Physical and Inorganic Chemistry; AII, Organic Chemistry; AIII, Physiology and Biochemistry, including Anatomy.

(*c*) *Annual Reports on the Progress of Chemistry.* These reports, written by experts, summarise the important new advances in pure chemistry and related subjects.

LIBRARY

The extensive reference and lending library of the Chemical Society contains over 44,000 volumes dealing with every aspect of Chemistry and with many branches of related sciences. The Library is open on week-days from 10 a.m. to 5 p.m., but for the present is closed on Saturdays.

MEETINGS

(*a*) *In London.*

Scientific Meetings of the Society are held usually on the first and third Thursdays of each month from October to June at Burlington House, at which papers dealing with original work are read and discussed, organised discussions on subjects of current interest are arranged, and lectures by eminent British and foreign chemists are delivered.

(*b*) *Outside London.*

Scientific Meetings and lectures are also held outside London, and form an important part of the activities of the Society in the Provinces.

RESEARCH FUND

A Research Fund is available for the assistance of chemical research, and sums amounting annually to about £700 are granted for this purpose. Application for grants must be made before the 1st November on the appropriate form, which may be obtained from the General Secretary.

Forms of Application for Fellowship can be obtained from THE GENERAL SECRETARY, THE CHEMICAL SOCIETY, BURLINGTON HOUSE, PICCADILLY, LONDON, W.1.

CHINA CLAYS (Kaolin)
BALL CLAY (Argile)
CORNWALL STONE (China Stone)
FELSPAR · KALYTES (Barytes Substitute)
ALUMINIUM SILICATE (Talc Substitute)
BENTONITE (and British Substitutes)
TALC (and British Substitutes)
QUARTZ SANDS
REFRACTORY CLAYS, BRICKS, TILES, etc. and other products.

for use in the manufacture of

Paper
Textiles
Earthenware
Porcelain
Refractories
Crucibles
Furnace Linings
Furnace Moulds
Insulators
Cement
Stoneware
Glass
Fuses
Paints
Enamels
Rubber Goods
Cables
Ultramarine
Inks
Insecticides
Matches
Fireworks
Medicines
Poultices
Cosmetics
Polishes
Roofing Felts
Soaps
etc.

THERE ARE MANY TYPES OF CHINA CLAY, BALL CLAY, etc., EACH HAVING ITS OWN PECULIARITIES. THEY DIFFER IN ANALYSES, PARTICLE SIZE, COLOUR, SUSPENSION, etc. They can be supplied in bulk or in finest powder form.

- ***Let us know what you are seeking***

and we will make recommendations and supply copious samples for tests.

Our British substitutes for foreign minerals are in daily increasing demand.

- *A few of our SPECIAL KAOLINS supplied in the finest powder form :*

STOCKALITE
DEVOLITE
COLWHITE
SPESWHITE
SUPREME

- *TALC SUBSTITUTES :* **TAKOLIN · TAKOLITE, Etc.**
- *BARYTES SUBSTITUTE :* **KALYTES**

PRODUCERS :

ENGLISH CLAYS LOVERING POCHIN & CO. LTD.

HEAD OFFICE, MINES and MILLS at

ST. AUSTELL CORNWALL

Offices also at London, Stoke, Manchester, Newcastle, Edinburgh, etc.
Depots and Stores in many parts of the country.

Telegrams : Universal, St. Austell. **'Phone : 482 St. Austell.**

NOTICES TO AUTHORS OF PAPERS

1. All Scientific Communications for the Journal should be addressed to "The Secretaries, Chemical Society, Burlington House, W.1." Papers to be read before a meeting of the Society are selected by the Secretaries.

2. A paper is not normally considered for publication in the Journal unless at least one of the authors is a Fellow of the Society, but in exceptional circumstances the Council is prepared to consider papers submitted by non-Fellows.

3. An author must submit with every paper a signed form of declaration that to the best of his knowledge the paper does not contain any information that contravenes the Official Secrets Act.

4. An author engaged in any Government Department or similar body associated with the prosecution of the war must submit with his paper a written declaration from such Department or body that he has received authority to submit the paper for consideration for publication in the Journal.

5. All papers should be submitted in typescript in double-line spacing. Footnotes in papers add considerably to the cost of printing; authors are requested, therefore, not to use them unless necessary.

6. Every paper should be prefaced by a short summary setting forth briefly and in simple language the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. The summary should be such as to enable any chemist to obtain a clear idea of what the investigation has achieved and should normally be from 50—250 words in length.

7. If he desires to do so, an author may send with the paper, for consideration by the Publication Committee, a confidential report by a Chemist of standing to whom the paper has been submitted.

8. The Publication Committee invites authors who publish series of related papers in the Journal to submit, at suitable intervals, papers reviewing their previously published work (suspended during the war).

9. The Society reserves the right to retain the Manuscript and illustrative drawings of all papers sent to it, and authors are therefore advised to keep copies. This right is not usually exercised in respect of illustrative drawings. When papers have been accepted for publication the authors are not at liberty, save by permission of the Council, to publish them elsewhere until such papers have appeared in the Journal of the Society. Papers which are retained by the Council after being judged unsuitable for publication in the Journal are deposited in the Archives of the Society.

10. Communications which have appeared in any other Journal shall not be published in the Journal of the Chemical Society unless this course is approved by a special vote of the Council.

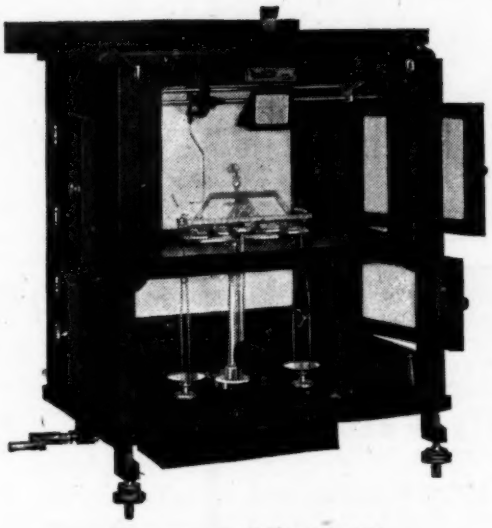
11. The address to which proofs are to be sent should be written on every paper.

12. Authors resident overseas are requested to name agents in Britain to whom may be referred matters concerning their papers, including the correction of proofs, in order that delay in publication may be avoided.

13. Illustrations accompanying the papers must be carefully drawn, preferably **twice** the size of the finished block (max. width, 4½ inches), **in Indian ink,** on **smooth white Bristol board or paper.** Any illustration which exceeds four times the size of the finished block will be returned to the author for re-drawing to a smaller scale. Lettering on the drawings, whether on the margin or in the body of the drawing, must not be in ink but must be inserted *lightly in blue pencil.* Authors may, if they wish, submit in the first place clearly drawn pencil sketches instead of the completed diagrams, which, however, must be supplied before publication. Further information can be obtained from Dr. C. Smith, Staplefield Grange Farm, Haywards Heath, Sussex.

14. If any Author requires more than the number of reprints (without wrappers) allowed by the Society, namely, 10 plus 10 extra for each author in excess of one, or desires to receive his reprints in wrappers and is willing to pay the extra cost thereby involved, he should inform Dr. Smith at the time he sends in the corrected proof. Extra copies will be supplied at rates which can be obtained from the Editor.

Reliable MICRO-CHEMICAL BALANCES



Please request specification No. 63 P.B.

BRITISH PRECISION BALANCES & WEIGHTS

We were pioneers in the design and manufacture of British Balances for the now exceedingly important micro-analytical technique. Even before the war, our micro and semi-micro balances were preferred by leading micro chemists, whose co-operation has been extremely valuable in perfecting a design at once quick and easy to read, sturdy and reliable. As a result Britain can now claim a leading place in the design of micro-balances—a position we hope, by our vigorous development policy, to maintain.

L. OERTLING LTD.,
ELLERDALE ROAD,
LONDON, N.W.3

Oertling
FOUNDED IN LONDON BEFORE 1847

TAS/OR. 203

VITREOSIL

ALWAYS RELIABLE
READILY OBTAINABLE

No user need fear shortage of supplies of VITREOSIL, pure fused silica. A large variety of acid and heat-proof ware is available for the laboratory or the works.

THE THERMAL SYNDICATE LTD.
Head Office: Wallsend, Northumberland
London Depot: 12–14 Old Pye St., Westminster, S.W.1
Established over 30 years

WRITE FOR SAMPLES and TECHNICAL INFORMATION..

PURE CRYSTAL **ALUM** OF UNVARYING COMPOSITION & UNRIVALLED PURITY

SULPHATE OF ALUMINA ALL GRADES SUPPLIED

"ALUMINOFERRIC" THE CHEAPEST FORM OF SULPHATE OF ALUMINA

ACTIVATED ALUMINA ADSORBENT AND CATALYST

SODIUM ALUMINATE HIGHEST QUALITY · FOR WATER SOFTENING

"NEOSYL" REGD (AMORPHOUS SILICA) UNIQUE LIGHTNESS & FINENESS

"TYPHOX" AND TITANIUM POTASSIUM OXALATE IDEAL MORDANTS FOR LEATHER DYEING

TITANOUS SULPHATE A MOST POWERFUL & ECONOMICAL STRIPPING AGENT

PETER SPENCE & SONS LTD
NATIONAL BUILDINGS · MANCHESTER 3
LONDON OFFICE: 4 HANGER GREEN · EALING · W5

Ⓡ G1.

L. LIGHT & Co. LTD
WRAYSBURY

ETHYLENE DIAMINE	PHENYLHYDRAZINE
PROPIOPHENONE	PHENANTHRENE
NITROMETHANE	TRIETHYLAMINE
N-OCTANOL	N-DECANOL
CHRYSENE	DIPHENYL
DIOXAN	RETENE

FINE ORGANIC CHEMICALS

FOYLES
BOOKSELLERS TO THE WORLD
Large Department for Technical Books

New and Secondhand Books on Chemistry and Every Other Subject. Stock of nearly 3 million volumes. Books Bought.

119–125 CHARING CROSS ROAD
LONDON, W.C.2
Open 9 a.m.—4 p.m. including Saturday.
Telephone: GERrard 5660 (16 lines).

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND

Founded 1877. Incorporated by Royal Charter, 1885.

APPOINTMENTS REGISTER.—A Register of Chemists (Fellows, Associates and Senior Registered Students) who are available for appointments, or who are seeking to improve their positions, is kept at the office of the Institute. The facilities afforded by this Register are available (free) to Companies and Firms requiring the services of Chemists, and to Universities, Colleges and Technical Schools requiring Teachers of Chemistry and Technology. A List of Laboratory Assistants is also available.

Particulars of the Regulations and Examinations of the Institute can be obtained (free) on application to the Registrar.

All communications to be addressed to—

The Registrar, The Institute of Chemistry, 30, Russell Square, London, W.C.1

FINE CHEMICALS

Purine Derivatives

Uric acid, Allantoin,
Alloxan, Alloxantin, Urethane

Allyl Derivatives

Allylamine, Allyl thiourea,
Allyl isothiocyanate

Urea and Derivatives

Urea, Phenyl urea, Selenourea,
Phenyl semicarbazide,
p-Phenetyl carbamide

Organic Sulphur Compounds

Thiophosgene, Thiocarbonyl tetrachloride,
S-Benzyl thiuronium chloride,
2-Methyl-β-naphthathiazole

also

Sodium cyanate (Pure and Practical)
s-Trinitrobenzene (Indicator)
Dihydroxyanthranol—1 : 2
Phloroglucinol
Dithranol—1 : 8
Rubidium salts
Nicotinic acid

HYDRAZINE SULPHATE

Enquiries invited from firms engaged on work of national importance.

Produced under strict scientific control and conforming to the highest standards. Data and Prices on request.

GENATOSAN LTD., LOUGHBOROUGH, LEICS.

TO
MEDICAL OFFICERS
NURSES
FIRST AID POSTS

WOUNDS, BURNS etc.
HEAL RAPIDLY and
WILL NOT TURN SEPTIC
IF TREATED WITH

ANTIPEOL OINTMENT

CUTANEOUS VACCINE

BECAUSE one or other or all of the three races of germs, Streptococci, Staphylococci, and B. pyocyaneus are found in every skin infection common to this country, and ANTIPEOL OINTMENT contains the *antibodies* (antivirus) of these germs. Healing is expedited by the proved ingredients of the ointment, and septic development is stopped or prevented by its antivirus sterile vaccine filtrates. ANTIPEOL OINTMENT is unsurpassed for BURNS and SCALDS, for it is microbicide and non-adhesive, and dressings do not require to be changed every day.

RHINO-ANTIPEOL

affords rapid relief of COMMON COLDS, INFLUENZA, AND CATARRH. Containing the antibodies of the germs common to infections of the nose and pharynx (Staphylococci, Streptococci, B. pyocyaneus, pneumococci, pneumobacilli, enterococci, M. catarrhalis, B. Pfeiffer), Rhino-Antipeol is not just a palliative, but is a remover of the *cause* of the infection. During epidemics it is the ideal preventive of microbic development.

OPHTHALMO-ANTIPEOL

is a semi-fluid ointment, more convenient than the ordinary Antipeol ointment for ocular infections and lesions. Eyes affected by smoke and dust are soothed almost immediately by the application of Ophthalmo-Antipeol, and the antivirus prevents germs from developing.

Clinical Samples on request from
MEDICO-BIOLOGICAL LABORATORIES LTD.
CARGREEN ROAD, SOUTH NORWOOD, LONDON, S.E.25

PYREX

Regd. Trade Mark. Brand

SCIENTIFIC GLASSWARE

is effective and dependable!

Normal dispensary requirements demand that the glassware in use should be not only resistant to sudden temperature changes but also able to resist attacks from acids, at the same time being sufficiently robust to withstand continuous everyday handling.

The additional sturdy strength made possible by the heat-resisting nature of PYREX Brand Scientific Glassware gives it a margin of safety in all experimental work carried out by the research chemist, effectively reduces the risk of breakage, and thus saves much of the heavy cost of glassware replacements.

PYREX Brand Scientific Glassware is absolutely dependable, and maintains, over a long period, the many vital and reliable characteristics by which it has become famous throughout the country.

• • • •

PYREX Brand Scientific Glassware is supplied only through Laboratory Furnishers, but illustrated catalogue and two free copies of our Chemist's Notebook will be sent direct on application to us.

Ask for PYREX Brand and see that you get it!

James A. Jobling & Co. Ltd.

SUNDERLAND.

T.17.B.

The Crack Pulverising Mills Ltd.

GRINDERS TO THE TRADE FOR

DRUGS, GUMS, SPICES and CHEMICALS

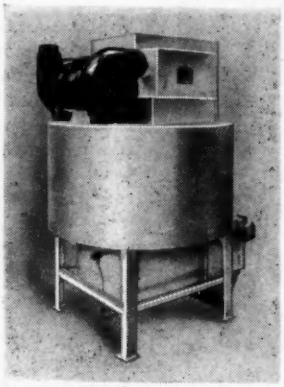
Expert Staff available for Reconditioning of Gums, Drugs, etc., Damaged by Fire or Water.

Address all communications to—

"THE HAWTHORNS," LEATHERHEAD ROAD, BOOKHAM (SURREY)

Works: Tannery Lane, Send, nr. Woking (Surrey). **Phone: BOOKHAM 2748**

BIRLEC C 50 LECTRO-DRYER



This gas-heated continuous type drying unit has an output of 500 c.f.m. dehumidified air, with an input moisture content of 4 gns./c.ft.^{3} (a typical summer humidity). It will give an output as low as 1 gn./ft.^{3}. This unit is particularly suitable for such applications as the conditioning of rooms handling or storing hygroscopic materials. Write to us for our special booklet on BIRLEC LECTRODRYERS.

BIRLEC

BIRMINGHAM ELECTRIC FURNACES LIMITED

ERDINGTON, BIRMINGHAM

LESSING CONTACT RINGS

for packing

Fractionating Columns

Absorbers

Catalyst Vessels

Combustion Tubes

MADE IN

ALL METALS

PORCELAIN

CHEMICAL STONEWARE

CARBON

Sizes from $\frac{1}{8}$" × $\frac{1}{8}$" to 4" × 4"

Tell us your problems

THE HYDRONYL SYNDICATE LTD.

14 Gloucester Road

London, S.W.7

SCIENTIFIC BOOKS

Books on the *Chemical* and Allied Sciences supplied from stock, or obtained promptly to order.

Please state interests when writing.

***Foreign Books* not in stock obtained under Licence.**

A wide selection of *Second-hand Books* may be seen at *140 Gower Street*.

H. K. LEWIS & Co. Ltd.

136 GOWER STREET, LONDON, W.C.1

Telegrams: 'Publicavit, Westcent, London.' *Telephone: EUSton 4282 (5 lines).*

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

Organic.

PAGE

157. Studies in the Polyene Series. Part V. The Employment of 3-(2′ : 6′ : 6′-Trimethyl*cyclo*hexenyl)-1-methylcrotonaldehyde for the Synthesis of Vitamin A and Analogues.
By I. M. Heilbron, A. W. Johnson, E. R. H. Jones, and A. Spinks 727

158. Studies in the Polyene Series. Part VI. The Preparation of Ethinylcarbinols from αβ-Unsaturated Aldehydes.
By E. R. H. Jones and J. T. McCombie 733

159. Studies in the Polyene Series. Part VII. Carbinols from Propargyl Acetal.
By I. M. Heilbron, E. R. H. Jones, and H. P. Koch 735

160. The Synthetic Application of *o*-β-Bromoethylbenzyl Bromide. Part I. Sulphanilamide Derivatives of 1 : 2 : 3 : 4-Tetrahydro*iso*quinoline.
By Frederick G. Holliman and Frederick G. Mann 737

161. Sapogenins. Part XVII. The Position of the Carboxyl Group in Oleanolic and Glycyrrhetic Acids.
By George A. R. Kon and Walter C. J. Ross 741

162. The Preparation of Symmetrical Azo-compounds, the Positional Influence of the Nitro-group on the Decomposition of Nitronaphthalenediazonium Sulphates by Cuprous Hydroxide, and an Improved Method for the Production of 2-Nitronaphthalene.
By Herbert H. Hodgson, Eric Leigh, and Gerald Turner 744

163. The Influence of *p*-Substituents on the Decomposition of Zinc Chloride Double Salts of Diazonium Chlorides by Acetic Anhydride.
By Herbert H. Hodgson and Clifford K. Foster 747

164. The Action of Cuprous Oxide on Diazotised Amines in Ethyl-alcoholic Acid Solution.
By Herbert H. Hodgson and Harold S. Turner 748

165. Studies on Agar-agar. Part III. Isolation of Hepta-acetyl *dl*-Galactose from 3 : 6-Anhydro-β-methyl-*d*-galactoside.
By T. L. Cottrell and E. G. V. Percival 749

166. Studies on Agar-agar. Part IV.
By E. G. V. Percival and T. G. H. Thomson 750

167. *p*-Aminodimethylaniline. Part II. The *o*-Chloro- and -Nitro-derivatives.
By Ernest E. Ayling, John H. Gorvin, and Leonard E. Hinkel 755

Note.—Some Quinoline Derivatives of Sulphanilamide.
By O. G. Backeberg and J. L. C. Marais 758

INDEX OF AUTHORS' NAMES.

Ayling, E. E., Gorvin, J. H., and Hinkel, L. E., 755.
Backeberg, O. G., and Marais, J. L. C., 758.
Cottrell, T. L., and Percival, E. G. V., 749.
Foster, C. K. See Hodgson, H. H.
Gorvin, J. H. See Ayling, E. E.
Heilbron, I. M., Johnson, A. W., Jones, E. R. H., and Spinks, A., 727.
Heilbron, I. M., Jones, E. R. H., and Koch, H. P., 735.
Hinkel, L. E. See Ayling, E. E.
Hodgson, H. H., and Foster, C. K., 747.
Hodgson, H. H., Leigh, E., and Turner, G., 744.
Hodgson, H. H., and Turner, H. S., 748.
Holliman, F. G., and Mann, F. G., 737.
Johnson, A. W. See Heilbron, I. M.
Jones, E. R. H., and McCombie, J. T., 733.
Jones, E. R. H. See also Heilbron, I. M.
Koch, H. P. See Heilbron, I. M.
Kon, G. A. R., and Ross, W. C. J., 741.
Leigh, E. See Hodgson, H. H.
McCombie, J. T. See Jones, E. R. H.
Mann, F. G. See Holliman, F. G.
Marais, J. L. C. See Backeberg, O. G.
Percival, E. G. V., and Thomson, T. G. H., 750.
Percival, E. G. V. See also Cottrell, T. L.
Ross, W. C. J. See Kon, G. A. R.
Spinks, A. See Heilbron, I. M.
Thomson, T. G. H. See Percival, E. G. V.
Turner, G. See Hodgson, H. H.
Turner, H. S. See Hodgson, H. H.

ERRATA.

VOL., 1942.

Page	Line	
363	3 *	*for* " 225° " *read* " 22·5°."
364		*for the entry under* " β-Iodopentane " *substitute the following :*

0·00000	2·2350	1·5940	28·14	128	28·1
0·00664	2·2722	1·5932	28·81	127	28·2
0·01147	2·2991	1·5928	29·28	126	28·2
0·02051	2·3489	1·5916	30·15	124	28·2
0·03930	2·4534	1·5893	31·95	122	28·3
0·08770	2·7227	1·5838	36·32	115	29
0·18527	3·276	1·5730	44·44	105	31
0·41776	4·568	1·5502	60·38	93	36
1·00000	7·249	1·5020	89·09	89·1	46

579	10	*for* " carbon atom 2 " *read* " carbon atom 3."
585	6—8	*substitute the following :* Nitric acid, *d* 1·42, expelled two methyl groups from 3 : 3′ : 5 : 5′-tetranitrotetramethylbenzidine; the 3 : 3′ : 5 : 5′-tetranitrodimethylbenzidine formed crystallised rapidly from hot nitrobenzene in deep yellow pyramids, m. p. 215° (decomp.) (Mertens, *Ber.*, 1886, **19**, 2125, gives red needles from phenol which decompose above 200°) (Found : N, 21·6. Calc. : N, 21·4%). Nitric acid, *d* 1·5, however, gave rise to *N* : *N*′ : 3 : 3′ : 5 : 5′-hexanitrodimethylbenzidine, which crystallised rapidly from hot nitrobenzene in bright yellow, lenticular or rhomboidal plates, m. p. 227° (decomp.), which explode in the flame (Mertens, *loc. cit.*, and Van Romburgh, *Rec. Trav. chim.*, 1886, **5**, 240, describe the compound as exploding above 220°).

* From bottom.

2 : 4 : 5-*Trinitro*-1-*naphthylamine*, obtained by hydrolysis of the above naphthalide (2·5 g.) with sulphuric acid (8 c.c., *d* 1·84) at 50—60°, the orange-brown solution being poured on ice, crystallised from aqueous pyridine in golden-yellow plates, m. p. 310° (Rindl, J., 1913, **103**, 1915, gives m. p. 305°, and Talen, *Rec. Trav. chim.*, 1928, **47**, 355, gives m. p. 310°) (Found : N, 20·5. Calc. : N, 20·2%).

The authors thank I.C.I. (Dyestuffs) Ltd. for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, July 11th*, 1942.]

---

156. *Cleavage of the Ethylene Linkage by the Action of Thionyl Chloride.*

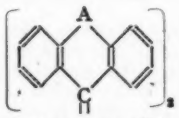
By ALEXANDER SCHÖNBERG and (MISS) WAFFIA ASKER.

Dixanthylene (I), dithioxanthylene (II), *NN'*-dimethyldiacridine (III), diflavylene (IV), and dithioflavylene (V) are cleaved by the action of thionyl chloride, followed by that of water, to the corresponding ketones; *e.g.*, xanthone (VIII) is formed from dixanthylene (I), and flavone (XI) from diflavylene (IV).

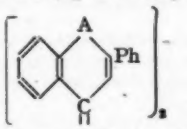
SCHÖNBERG (*Ber.*, 1925, **58**, 7096) showed that dixanthylene (I), when treated with sulphur, yielded xanthione (VI), which was the first example of the cleavage of the ethylene linkage by sulphur with the formation of a thioketone. Recently (this vol., p. 272) the authors have shown that a similar reaction takes place with dithioxanthylene (II), diflavylene (IV), and dithioflavylene (V).

We have now found that the ethylene linkage in (I), (II), (III), (IV), and (V) can also be easily split by refluxing these substances with thionyl chloride for one hour; *e.g.*, dixanthylene (I) gives an oil which on short treatment with water at 30° yields xanthone in practically quantitative yield. If aniline is used instead of water, xanthoneanil is obtained. *NN'*-Dimethyldiacridine (III), which reacts with sulphur with formation of *N*-methylthioacridone (VII) (Gleu and Schaarschmidt, *Ber.*, 1939, **72**, 1246), gives *N*-methylacridone (X) when treated with thionyl chloride and then with water.

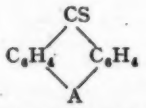
Tetraphenylethylene, when treated with thionyl chloride and water, is practically unchanged.



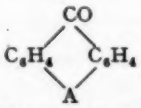
(I, A = O; II, A = S; III, A = NMe.)



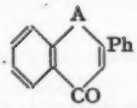
(IV, A = O; V, A = S.)



(VI, A = O; VII, A = NMe.)



(VIII, A = O; IX, A = S; X, A = NMe.)



(XI, A = O; XII, A = S.)

EXPERIMENTAL.

Xanthone (VIII) *from Dixanthylene* (I).—Dixanthylene (0·5 g.) was refluxed with thionyl chloride (25 c.c.) for 1 hour, the excess of thionyl chloride distilled off completely (pump), and the residual orange oil dissolved in benzene and shaken with water at 30° for 10 mins. The benzene layer was evaporated, and the residual yellowish-white xanthone crystallised from alcohol; the mother-liquor also contained pure xanthone. The yield was practically quantitative.

Xanthoneanil from Dixanthylene.—Dixanthylene (1 g.) was refluxed with thionyl chloride (50 c.c.) for 1 hour, the excess of thionyl chloride distilled off, and the residual oil dissolved in dry benzene (30 c.c.) and refluxed with aniline (2 g.) for 1 hour. The mixture was evaporated to dryness, and dilute hydrochloric acid added to the residue. Xanthoneanil was extracted with ether and crystallised from light petroleum; it did not depress the m. p. of an authentic specimen (Schönberg and Schütz, *Annalen*, 1927, **454**, 51).

Thioxanthone (IX) *from Dithioxanthylene* (II).—The reaction was carried out as described in the case of dixanthylene, and the thioxanthone obtained crystallised from benzene. It did not depress the m. p. of an authentic specimen (Gomberg and Britton, *J. Amer. Chem. Soc.*, 1921, **43**, 1946).

Flavone (XI) *from Diflavylene* (IV).—Diflavylene (Schönberg, *Ber.*, 1931, **64**, 2326) was treated with thionyl chloride and water as described above. Flavone thus obtained was crystallised from light petroleum. It gave no depression of m. p. with an authentic specimen (Löwenbein, *Ber.*, 1924, **57**, 1516).

N-*Methylacridone* (X) *from* NN'-*Dimethyldiacridine* (III).—The diacridine (Decker and Petsch, *J. pr. Chem.*, 1935, **143**, 227) (0·5 g.) was treated with thionyl chloride for 12 hours, the excess of thionyl chloride distilled off, and the yellow solid treated with water as described above. The product was crystallised from alcohol; it did not depress the m. p. of *N*-methylacridone (Decker and Petsch, *loc. cit.*, p. 222).

FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, August 17th*, 1942.]

NOTES.

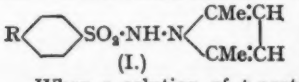
Some Anilinopyridine Derivatives. By WILLIAM O. KERMACK and (MISS) ALICE P. WEATHERHEAD.

THE following anilinopyridine derivatives have been prepared with the object of obtaining 2 : 3-pyridoquinolines (pyracridines): *2-Anilinonicotinic acid*, from 2-chloronicotinic acid and aniline at 160° for 1 hour, recrystallised from alcohol, formed almost colourless plates, m. p. 263° (Found: N, 13·0. $C_{12}H_{10}O_2N_2$ requires N, 13·1%). *2-p-Anisidinonicotinic acid*, from 2-chloronicotinic acid and *p*-anisidine at 150° for 1 hour, recrystallised from alcohol, formed faintly purple plates, m. p. 295° (Found: N, 11·4. $C_{13}H_{12}O_3N_2$ requires N, 11·5%). *4-Anilinopyridine*, from 4-chloropyridine and aniline at 150° for 2 hours, recrystallised from benzene, formed white needles, m. p. 173° (Found: N, 16·4. $C_{11}H_{10}N_2$ requires N, 16·5%). *N-(4'-Pyridyl)anthranilic acid hydrochloride*, from 4-chloropyridine and anthranilic acid in glacial acetic acid at 120° for 3 hours, recrystallised from alcohol, formed white needles, m. p. 185° (Found: N, 11·4. $C_{12}H_{10}O_2N_2$,HCl requires N, 11·2%). *N-(3'-Pyridyl)anthranilic acid*, from 3-aminopyridine and potassium *o*-bromobenzoate in amyl alcohol with a trace of copper bronze at 130° for 6 hours, recrystallised from alcohol in small cubes, m. p. 238° (Found: C, 67·1; H, 4·5. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·6%).

All attempts to cyclise the above carboxylic acids by treatment with sulphuric acid or phosphoryl chloride have so far failed.—RESEARCH LABORATORY, ROYAL COLLEGE OF PHYSICIANS, EDINBURGH. [*Received, October 2nd*, 1942.]

The Preparation of 1-p-*Aminobenzenesulphonamido*-2 : 5-*dimethylpyrrole.* By E. O'FARRELL WALSH.

ACETONYLACETONE condenses with *p*-acetamidobenzenesulphonhydrazide in hot glacial acetic acid to give 1-*p*-acetamidobenzenesulphonamido-2 : 5-dimethylpyrrole in theoretical yield. The product on alkaline hydrolysis yields 1-p-*aminobenzenesulphonamido*-2 : 5-*dimethylpyrrole* (I, R = NH_2), which, it is suggested, may be of therapeutic value. It is essential that pure sulphonhydrazide, free from traces of sulphonyl chloride, be used for the condensation, otherwise uncrystallisable red tars are produced.



(I.)

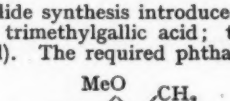
When a solution of *p*-acetamidobenzenesulphonhydrazide (6 g.) in boiling glacial acetic acid (15 c.c.) containing acetonylacetone (4 c.c.) is heated for a few minutes, crystals begin to separate. The hot solution is diluted with warm water and cooled rapidly, and the crystals separated immediately, washed with cold water, and dried. Yield 8 g., m. p. 240° (decomp.). Deacetylation is effected by refluxing with 20% sodium hydroxide solution until a test portion gives no precipitate with excess of acid (1—1½ hrs.). The solution is diluted, acidified with acetic acid, and neutralised with ammonia; the *sulphanilamide* derivative (I, R = NH_2) thus precipitated in 85% yield crystallises from aqueous alcohol in colourless platelets, m. p. 202° (decomp.) (Found: N, 15·8; S, 11·9. $C_{12}H_{15}O_2N_3S$ requires N, 15·85; S, 12·1%).

1-p-*Toluenesulphonamido*-2 : 5-*dimethylpyrrole* (I, R = Me), prepared by the above method from *p*-toluenesulphonhydrazide, crystallises from acetic acid or aqueous alcohol in large needles, m. p. 144°, readily soluble in alcohol, acetone, and acetic acid, soluble in chloroform, sparingly in ether, and insoluble in light petroleum (Found: N, 10·6. $C_{13}H_{16}O_2N_2S$ requires N, 10·6%).

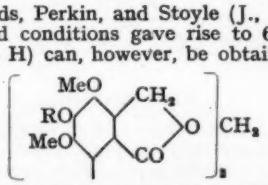
I am indebted to Mr. J. E. Still for the micro-analyses for nitrogen and sulphur.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, September 18th*, 1942.]

Synthesis of Phthalides from 3 : 4 : 5-*Trimethoxybenzoic Acid.* By F. E. KING and T. J. KING.

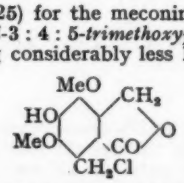
THE phthalide synthesis introduced by Edwards, Perkin, and Stoyle (J., 1925, **127**, 125) for the meconines has been applied to trimethylgallic acid; the published conditions gave rise to 6-*chloromethyl*-3 : 4 : 5-*trimethoxyphthalide* (I, R = CH_2Cl). The required phthalide (I, R = H) can, however, be obtained by using considerably less hydrochloric



(I.)



(II).



(III.)

acid, and it was identified by comparison with a specimen prepared by the Fritsche method from the gallic acid, chloral, and sulphuric acid (Alimchandani and Meldrum, J., 1920, **117**, 964). From the formaldehyde reaction a small quantity of the phthalide (II, R = Me) was also isolated.

Before the constitution of the compound (I, R = CH_2Cl) had been ascertained, there was a possibility that it arose from syringic acid formed by demethylation with hot mineral acid, but syringic acid actually gave the *chloromethylphthalide* (III), together with 6 : 6'-*methylenebis*-4-*hydroxy*-3 : 5-*dimethoxyphthalide* (II, R = H), which when methylated gave (II, R = Me).

In pyrogallolcarboxylic acid 3 : 4-dimethyl ether the *o*-position is less active, and the formaldehyde–hydrochloric acid reaction gave only 5 : 5'-*methylenebis*-2-*hydroxy*-3 : 4-*dimethoxybenzoic acid*.

3 : 4 : 5-Trimethoxyphthalide reacted with sodium ethoxide and ethyl oxalate, giving *ethyl* 3 : 4 : 5-*trimethoxyphthalidylglyoxylate*, which was conveniently isolated as its sodium salt.

6-*Chloromethyl*-3 : 4 : 5-*trimethoxyphthalide* (I, R = CH_2Cl).—A mixture of trimethylgallic acid (10 g.), aqueous formaldehyde (25 c.c. of 40%), and concentrated hydrochloric acid (40 c.c.) was refluxed for 20 minutes in an oil-bath at 140°. On cooling and addition of water, the oily product solidified; recrystallisation from alcohol gave the *chloromethylphthalide* (7 g.) in colourless needles, m. p. 85°, with marked irritant properties (Found: C, 52·8; H, 4·8. $C_{12}H_{13}O_5Cl$ requires C, 52·8; H, 4·8%).

3 : 4 : 5-*Trimethoxyphthalide* (I, R = H).—When the previous experiment was repeated with a smaller amount of hydrochloric acid (10—12 c.c.), the product was 3 : 4 : 5-trimethoxyphthalide, which by two crystallisations from alcohol (charcoal) was obtained in colourless prisms (5·5 g.), m. p. 134—135° alone or mixed with an authentic specimen (Alimchandani and Meldrum, *loc. cit.*). Heating the phthalide (1 g.) with formalin (2·5 c.c. of 40%) and excess of concentrated hydrochloric acid (4—5 c.c.) for 30 minutes gave the above chloromethyl derivative, m. p. and mixed m. p. 85°.

6 : 6'-*Methylenebis*-3 : 4 : 5-*trimethoxyphthalide* (II, R = Me).—Once-crystallised specimens of the trimethoxyphthalide (I, R = H) or of its chloromethyl derivative (I, R = CH_2Cl) were treated with boiling alcohol, and the solutions quickly decanted from the sparingly soluble residue (yield, *ca.* 5%). Recrystallisation from alcohol gave the *methylenebisphthalide* in pointed prisms, m. p. 199° (Found: C, 59·5; H, 5·2. $C_{23}H_{24}O_{10}$ requires C, 60·0; H, 5·2%).

6 : 6′-Methylenebis-4-hydroxy-3 : 5-dimethoxyphthalide (*vide infra*) (0·5 g.) was refluxed with potassium carbonate (1 g.) and methyl iodide (2 c.c.) in acetone (20 c.c.) for 8 hours. The product, isolated by evaporation of the solvent and addition of water, when crystallised from alcohol had m. p. and mixed m. p. 199°.

6-*Chloromethyl*-4-*hydroxy*-3 : 5-*dimethoxyphthalide* (III).—The clear solution obtained by heating syringic acid (10 g.) for 10—12 minutes with aqueous formaldehyde (25 c.c. of 40%) and concentrated hydrochloric acid (40 c.c.) on a steam-bath, slowly deposited a dark oil which shortly solidified. The product collected after 30 minutes' heating crystallised from alcohol in long rectangular tablets of the *chloromethylphthalide*, m. p. 185° (Found : C, 50·7; H, 4·3. $C_{11}H_{11}O_5Cl$ requires C, 51·1; H, 4·3%). The phthalide dissolved in aqueous sodium carbonate, giving a slowly fading pink colour; the ferric chloride reaction was a weak green-yellow.

6 : 6′-*Methylenebis*-4-*hydroxy*-3 : 5-*dimethoxyphthalide* (II, R = H).—The formaldehyde–acid solution from which the above phthalide (III) had been collected was diluted with water, and the resinous product crystallised from alcohol (charcoal). It formed opaque bipyramids, m. p. 223—224°, giving an olive-green ferric chloride reaction (Found : C, 58·5; H, 4·7. $C_{21}H_{20}O_{10}$ requires C, 58·3; H, 4·6%).

5 : 5′-*Methylenebis*-2-*hydroxy*-3 : 4-*dimethoxybenzoic Acid*.—Pyrogallolcarboxylic acid 3 : 4-dimethyl ether (5 g.) was heated for 30 minutes with concentrated hydrochloric acid (20 c.c.) and aqueous formaldehyde (12 c.c.) at 140°, and the product precipitated by water. Crystallisation from 80% alcohol gave minute needles, m. p. 252° (efferv.); these gave an intense blue ferric chloride reaction (Found : C, 55·3; H, 5·0. $C_{19}H_{22}O_{10}$ requires C, 55·6; H, 5·3%).

Ethyl 3 : 4 : 5-*Trimethoxyphthalidylglyoxylate*.—To a suspension of sodium ethoxide prepared from powdered sodium (1·6 g.) and alcohol (3·2 g.) in toluene (30 c.c.), freshly distilled ethyl oxalate was added. The trimethoxyphthalide (15 g.) was now introduced, and the mixture heated (hydrogen atmosphere) on a steam-bath for 2 hours. The bright yellow insoluble sodium salt of the *phthalidylglyoxylate* was collected from the dark green liquid, washed with ether, and the free ester obtained by trituration with ice-cold aqueous acetic acid. Crystallisation from ethyl acetate–acetic acid gave pale yellow prisms, m. p. 188—189°, exhibiting a steel-blue ferric chloride reaction (Found : C, 55·6; H, 5·1. $C_{15}H_{16}O_8$ requires C, 55·5; H, 4·9%).—Dyson Perrins Laboratory, Oxford. [*Received, August 19th*, 1942.]

---

157. *Studies in the Polyene Series. Part V. The Employment of* 3-(2′ : 6′ : 6′-*Trimethylcyclohexenyl*)-1-*methylcrotonaldehyde for the Synthesis of Vitamin A and Analogues.*

By I. M. Heilbron, A. W. Johnson, E. R. H. Jones, and A. Spinks.

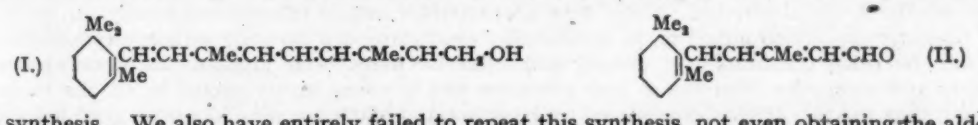
Previous work on the synthesis of vitamin A (I) is reviewed with particular reference to anomalies encountered in the use of β-ionone (III). A new scheme for the synthesis of vitamin A and analogues, based on the coupling of the aldehyde (V) with 3-ketobutanol through an acetylene molecule has been devised and this paper contains an account of preliminary work along these lines.

The preparation of *glycide* esters (VII, VIII, and IX) from β- and α-ionones and mesityl oxide is described. Light absorption data (Tables I and II) reveal that the epoxy-group in these compounds largely resembles an ethylenic linkage in absorptive properties. Decarboxylation of the glycide acids from β- and α-ionone yields isomeric αβ-unsaturated C_{14} *aldehydes* (V and X respectively), both of which have been characterised by the preparation of derivatives. Absorption spectra (Table III) of the latter and of the aldehydes themselves provide valuable constitutional evidence. The glycide acid (IX) from mesityl oxide on decarboxylation gives a mixture of 2 : 4-dimethylpentenals (XII and XIII), from which only derivatives of the αβ-unsaturated isomer (XII) are isolated.

The aldehyde (V) condenses with acetone, yielding the *ketone* (XIV), the value of which for the synthesis of vitamin A analogues is pointed out. This is emphasised by the successful condensation of the ketone with ethylmagnesium bromide to a C_{19} *carbinol* (XVII).

Preliminary experiments on the reaction of αβ-unsaturated aldehydes with acetylene led to the preparation of 1-*ethinylgeraniol* (XVIII) (from citral) and the *ethinylcarbinol* of (V), and indications of the successful dehydration of (XVIII) have been obtained.

Whereas the structure of vitamin A (I) has been definitely established by degradation experiments (Karrer, Morf, and Schopp, *Helv. Chim. Acta*, 1931, **14**, 1036, 1431; Heilbron, Morton, and Webster, *Biochem. J.*, 1932, **26**, 1194) and also by the synthesis of the perhydro-vitamin (Karrer and Morf, *Helv. Chim. Acta*, 1933, **16**, 625), the only claim to have synthesised the vitamin itself is that of Kuhn and Morris (*Ber.*, 1937, **70**, 853). This synthesis is based on the condensation of 2-methylcrotonaldehyde with β-ionylideneacetaldehyde (II), the latter being prepared by reduction of the *o*-toluidide of the corresponding β-ionylideneacetic acid by the successive actions of phosphorus pentachloride and chromous chloride (von Braun and Rudolph, *Ber.*, 1934, **67**, 1735). The final product was claimed to contain 7·5% of vitamin A as estimated by the antimony trichloride colour reaction and also by biological tests. No subsequent publication on this synthesis has emanated from the Heidelberg laboratories and both Karrer and Ruegger (*Helv. Chim. Acta*, 1940, **23**, 284) and Krauze and Slobodin (*J. Gen. Chem. Russ.*, 1940, **10**, 907) have reported unfavourably on the Kuhn and

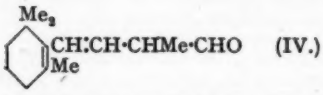


Morris synthesis. We also have entirely failed to repeat this synthesis, not even obtaining the aldehyde (II), and in this connection it is noteworthy that von Braun and Kurtz (*Ber.*, 1937, **70**, 1009) were unable to prepare citrylideneacetaldehyde from the corresponding acid by the series of reactions employed by Kuhn and Morris. That these authors obtained a final product possessing growth-promoting properties cannot be denied in view of the published results, but it is doubtful whether their material contained vitamin A as isolated

from natural sources, and further, it is clear that, since the formation of this biologically active substance by the series of reactions employed is apparently fortuitous, the synthesis is of little practical value.

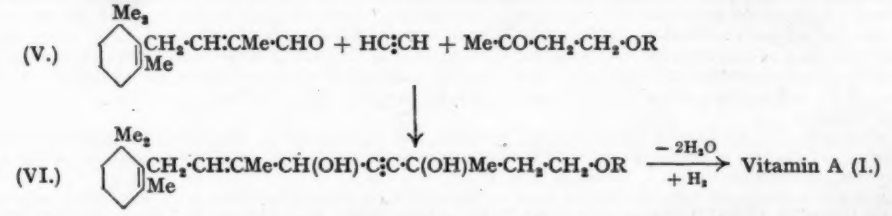
Kipping and Wild (*Chem. and Ind.*, 1939, **58**, 802) have reported a synthesis of vitamin A methyl ether by condensation of 6-methoxy-4-methylhexa-2 : 4-dienyl bromide with β-ionone of unspecified purity in the presence of lithium, followed by dehydration of the product. In the absence of any published criteria as to the nature of their final product (neither absorption spectra nor biological data are given) this claim can only be accepted with considerable reserve.

Although the most obvious starting material for the synthesis of vitamin A would appear to be β-ionone (III), apart from its normal Reformatsky reaction with ethyl bromoacetate and some evidence of normal reactions with vinylacetylenes, in general this ketone behaves anomalously (Gould and Thompson, *J. Amer. Chem. Soc.*, 1935, **57**, 340; Karrer, Salomon, Morf, and Walker, *Helv. Chim. Acta*, 1932, **15**, 878; Giacolone, *Gazzetta*, 1937, **67**, 464; Kipping and Wild, J., 1940, 1239), exhibiting a marked tendency towards the



formation of 1 : 4-adducts. According to Kipping and Wild (J., 1940, 1239) β-ionone reacts normally with methyl-lithium and phenyl-lithium. Prior to their publication we had attempted reactions in the presence of lithium with more complex halides (*e.g.*, hexadienyl and octatrienyl bromides, bromoacetal, etc.) but in no case could homogeneous products exhibiting the expected light absorption be isolated. In contrast to the abnormal behaviour of β-ionone, the α-isomer undergoes essentially 1 : 2-addition and consequently statements in the literature concerning normal reactions of the former must be accepted with reserve unless supported by definite evidence of purity of the starting material such as is provided by light absorption data, refractive index, etc. In our experience, no commercial specimen should be employed without purification through a derivative and the essential constants should be indicated.

In searching for routes to vitamin A or related compounds containing the necessary polyene system but not involving Grignard-type reactions with β-ionone, our attention became focused on the possibility of employing the aldehyde originally described by Ishikawa and Matsuura (*Sci. Rep. Tokyo Bunrika Daigaku, A*, 1937, **3**, 173; *Chem. Zentr.*, 1937, II, 3452) * and formulated by them as (IV) but now shown to be correctly represented by (V). This aldehyde is of especial interest, since it would be expected to react normally in all types of Grignard reaction and the broken conjugation readily lends itself to syntheses of polyenes involving acetylene condensations. Its value for vitamin A syntheses is clearly indicated in the following scheme :



It is obvious from the above that many alternative methods of effecting the completed project present themselves. Thus the glycol (VI) could be reached either (*a*) by the condensation of the ketonic portion with the ethinylcarbinol of (V) or alternatively (*b*) by the condensation of (V) with the ethinylcarbinol derived from an appropriate ketone. Further, the determination of the most suitable stage for the removal of water from the carbinols or glycols and for the semihydrogenation of the acetylenic bond leads to a multiplicity of permutations and combinations of the basic theme. The many implications of this scheme are in course of investigation in these laboratories and, as is inevitable, numerous new problems have arisen, the elucidation of which will form the subject of this and subsequent publications.

In the first place a more detailed study of the preparation and properties of the aldehyde prepared by Ishikawa and Matsuura (*loc. cit.*) appeared to be essential, as no evidence in support of its formulation as (IV) was provided. The Japanese authors condensed both α- and β-ionones (characterised only by their b. p.'s at different pressures) with ethyl chloroacetate and the glycide esters (obtained in 20% yields) were hydrolysed with alcoholic alkali to the glycide acids, which decomposed spontaneously on liberation from their salts, giving poor yields of the aldehydes. These were characterised as the thiosemicarbazones (m. p. 152° and 160° corr. respectively, but no mixed m. p. mentioned), which provided the only satisfactory analytical data in the paper. No other constants (*e.g.*, density and refractive index) were given to distinguish between the glycide esters and aldehydes from the α- and β-ionones and it seems highly probable, on the basis of our findings (*q.v.*), that the two aldehydes prepared by Ishikawa and Matsuura were identical, both being derived from α-ionone.

By interaction of β-ionone (regenerated from its crystalline semicarbazone) with ethyl chloroacetate in the presence of sodium methoxide at − 60° rather than at 0° (cf. Yarnall and Wallis, *J. Org. Chem.*, 1939, **4**,

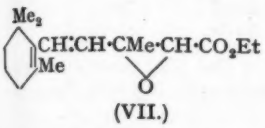
* The authors are indebted to Dr. W. E. Jones for drawing their attention to this paper.

270) a 60% yield of the *glycide* ester (VII) was obtained. Hydrolysis with alcoholic alkali furnished a crude acid which gave a small yield of a crystalline *glycide acid*, m. p. 132° (decomp.), yielding the *methyl* ester on

TABLE I.

From β-Ionone.	λ max., A.	log ε.
Glycide acid (m. p. 132°) (Fig. 1)	2870	4·49
Ethyl ester (Fig. 1)	2860	4·25
Methyl ester	2860	4·56

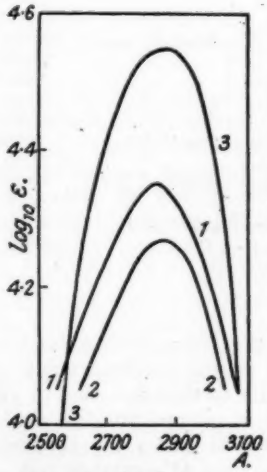
treatment with diazomethane. All three substances exhibit high intensity absorption at 2860 A. (Table I) which, at first sight, is not readily reconcilable with the formulation (VII). We have been unable to obtain evidence that the acid or its esters exist in the isomeric keto-form, *i.e.*, absence of coloration with ferric chloride, no evolution of methane with methylmagnesium iodide, and failure to exhibit ketonic reactions, and there is no escape from the hypothesis that the epoxy-group in compounds such as (VII) largely resembles, insofar as light absorption properties are concerned, an ethenoid linkage. Thus, whereas octatrienic acid, containing three double bonds conjugated with the carboxyl group, absorbs, in alcoholic solution, at 2960 A., sorbic acid absorbs only at 2540 A. in the same solvent (Smakula, *Angew. Chem.*, 1934, **47**, 657).



(VII.)

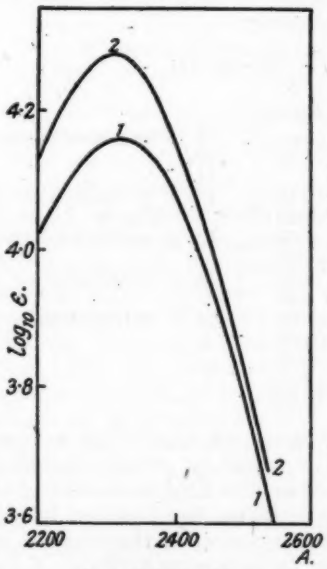
Although all three compounds listed in Table I were analytically pure, a marked difference in the intensities

FIG. 1.



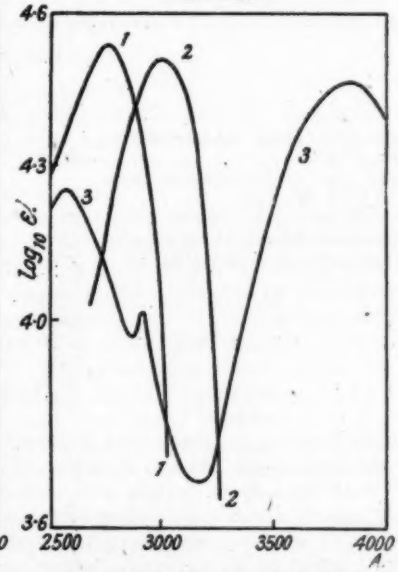
1. *Ketone* (XIV).
2. *Glycide ester* (VII).
3. *Acid corresponding to* (VII).

FIG. 2.



1. *Aldehyde* (X).
2. *Aldehyde* (V).

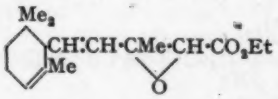
FIG. 3.

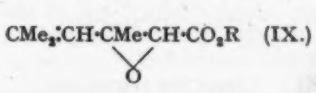


1. *Phenylsemicarbazone of aldehyde* (V).
2. *Thiosemicarbazone* ,, ,,
3. 2:4-*Dinitrophenylhydrazone* ,,

of the absorption at 2860 A. is apparent between the ethyl ester obtained directly from the condensation on the one hand, and the crystalline acid and the methyl ester derived from it on the other, a difference which is also clearly reflected in the divergent refractive indices of the two esters (see Experimental). A similar behaviour is also apparent in the case of the glycide esters from mesityl oxide (see Table II). These variations in the physical constants of analytically pure materials can only be ascribed to the existence of stereoisomeric forms of the glycide acid. Such marked intensity variations with stereoisomers are not unusual. Smakula and Wassermann (*Z. physikal. Chem.*, 1931, **155**, 353) observed more than 100% differences in intensity between the *cis*- and the *trans*-forms of both stilbene and cinnamic acid.

In order to obtain further spectrographic values for unsaturated glycide esters and also to study the aldehydes obtained on decarboxylation of the corresponding glycide acids, condensations of both α-ionone and mesityl oxide with ethyl chloroacetate have been carried out. The *glycide* ester (VIII) from α-ionone

(VIII.) 



(IX.)

was obtained in 30% yield but in this case the glycide acid failed to crystallise. Mesityl oxide gave a *glycide* ester (IX) (a mixture of methyl and ethyl esters was obtained, due to some alcoholysis with the sodium

methoxide employed as condensing agent) in 55% yield, which on hydrolysis yielded a small amount of a crystalline *glycide acid*, m. p. 72°, the latter furnishing a *methyl* ester on treatment with diazomethane. The light absorption data for these compounds are in Table II, from which two main facts emerge. The epoxy-group in compounds of the type of (VIII) and (IX) again resembles an ethylenic linkage, as has already

TABLE II.

	From α-ionone.		From mesityl oxide.		
	λ max., A.	log ε.		λ max., A.	log ε.
Glycide acid (crude) ...	2340	4·00	(m. p. 72°)	2345	4·025
			(crude)	2345	3·87
Ethyl ester	2340	4·06		2340	3·95
Methyl ester	—	—	(from cryst. acid)	2345	4·01
			(crude)	2345	3·91

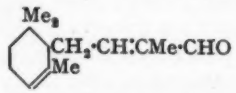
been suggested by the data in Table I. Secondly, in the case of the methyl ester of the acid corresponding to (IX) there is again apparent a very definite difference in the intensities of absorption of otherwise analytically pure samples.

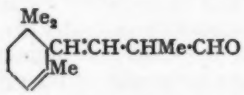
Numerous methods of decarboxylating the above glycide acids have been examined and heating with copper powder in a vacuum at about 130° produced the most satisfactory results. Under these conditions the crude acid corresponding to (VII) gave a 30% yield of the aldehyde (V), *i.e.*, 3-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-1-*methylcrotonaldehyde*, the αβ-unsaturated nature of which is illustrated by its absorption spectrum and also by similar data (Table III) for the *thiosemicarbazone* (from which the pure aldehyde was regenerated), *phenylsemicarbazone*, and 2 : 4-*dinitrophenylhydrazone*.

TABLE III.

	λ max., A.	log ε.		λ max., A.	log ε.
1. Aldehyde (V) (from thiosemicarbazone) (Fig. 2)	2800	4·25	9. Thiosemicarbazone of 1 (Fig. 3)	2990	4·59
2. Aldehyde (X) (from thiosemicarbazone) (Fig. 2)	2325	4·16	10. „ „ 2	3030	4·53
3. Aldehyde (XII + XIII) (crude) ...	2270	3·69	11. „ „ 4	3030	4·66
4. Citral (commercial sample distilled)	2320	4·05	12. 2 : 4-Dinitrophenylhydrazone of 1	3830	4·46
5. Phenylsemicarbazone of 1 (Fig. 3)	2780	4·57	(Fig. 3)	2580	4·25
	2370	4·34	13. 2 : 4-Dinitrophenylhydrazone of 2 ...	3840	4·46
6. „ „ 2	2775	4·53		2600	4·26
	2370	4·30	14. 2 : 4-Dinitrophenylhydrazone of (XII)	3820	4·49
7. „ „ (XII)	2750	4·50		2540	4·26
	2380	4·30	15. 2 : 4-Dinitrophenylhydrazone of 4	3840	4·52
8. „ „ 4	2850	4·64		2550	4·35
	2390	4·30			

Although there is no doubt that the derivatives are those of an αβ-unsaturated aldehyde, the possibility that the aldehyde itself has the structure (IV) cannot be entirely excluded on the spectrographic evidence, since (IV) contains a diene system which would exhibit light absorption similar to that recorded in Table III. We do not attach much importance to this possibility, but in order to provide more complete evidence for formulation (V) we have examined the decarboxylation of the isomeric glycide acid from α-ionone. This gave a 65% yield of an aldehyde, which we formulate as 3-(2′ : 6′-*trimethyl*-$\Delta^{2'}$-cyclo*hexenyl*)-1-*methylcrotonaldehyde* (X), and this has been characterised by the preparation and analysis of the *thiosemicarbazone* (from which the pure aldehyde was regenerated), *phenylsemicarbazone*, and the 2 : 4-*dinitrophenylhydrazone*. The light absorption data for this aldehyde and its derivatives (Table III) proved to be strictly analogous to

(X.) 



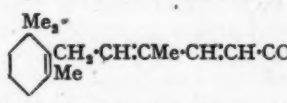
(XI.)

those obtained for the isomeric aldehyde (V) from β-ionone and, since the only alternative formulation (XI) contains no conjugated system, there is no doubt that the aldehydes obtained from β- and α-ionone are correctly represented by (V) and (X) respectively.

On heating the acid (IX, R = H) at 145°/760 mm. in the presence of copper powder an aldehyde was obtained in 35% yield. The molecular extinction coefficient (ε) of this aldehyde at its maximum is considerably lower than that observed for citral (see Table III) and this, together with the fact that, although crystalline aldehydic derivatives are readily formed, their purification is extremely tedious, suggests that

(XII.) $CHMe_2 \cdot CH{:}CMe \cdot CHO$

(XIII.) $CMe_2{:}CH \cdot CHMe \cdot CHO$

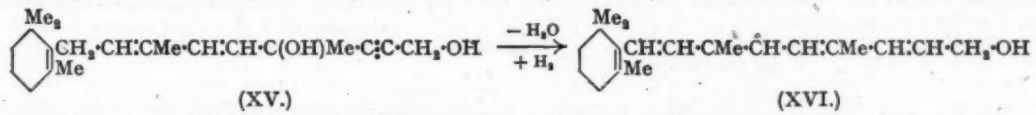


(XIV.)

this aldehyde is a mixture of the two 2 : 4-dimethylpentenals (XII) and (XIII), containing approximately 25% of the former. The *semicarbazone*, *phenylsemicarbazone*, and 2 : 4-*dinitrophenylhydrazone* must, from

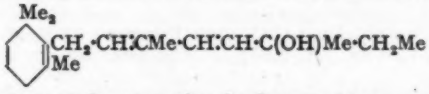
their absorption spectra (Table III), be derivatives of the αβ-unsaturated aldehyde (XII), *i.e.*, 2 : 4-dimethylpent-2-enal. An aldehyde of this constitution was described by Kohn (*Monatsh.*, 1901, **22**, 21), but no data were given whereby a direct comparison could be made. Regeneration from the partially purified semicarbazone gave an analytically pure aldehyde mixture richer in (XII) (maximum, 2270 A.; $\log \varepsilon = 3{\cdot}94$).

Condensation of the C_{14} aldehyde (V) with acetone has been effected in the presence of sodium ethoxide, or preferably aluminium *tert.*-butoxide, yielding a C_{17} ketone to which the constitution 7-(2′ : 6′ : 6′-*trimethylcyclohexenyl*)-5-*methylhepta*-3 : 5-*dien*-2-*one* (XIV) is ascribed. The ketone, purified through the crystalline *semicarbazone*, exhibited a single well-defined absorption maximum (Fig. 1) at 2850 A. ($\log \varepsilon = 4{\cdot}35$) comparing satisfactorily with that of ψ-ionone (max. 2930 A., $\log \varepsilon = 4{\cdot}37$), which contains the same chromophoric



(XV.) (XVI.)

group. This ketone (XIV) is of potential importance for the synthesis of polyenes of the vitamin A type. Thus condensation with propargyl alcohol or one of its derivatives by the Grignard or other method would furnish a primary-tertiary glycol (XV) which, on partial dehydration and semihydrogenation of the acetylenic bond, would yield an alcohol (XVI) differing from the vitamin only in the position of one of the side-chain methyl groups. In order to ascertain the practicability or otherwise of the initial condensation involved in this scheme the ketone has been treated with ethylmagnesium bromide; the carbinol, 8-(2′ : 6′ : 6′-*trimethylcyclohexenyl*)-3 : 6-*dimethylocta*-4 : 6-*dien*-3-*ol* (XVII), was then obtained, as shown by its absorption band at

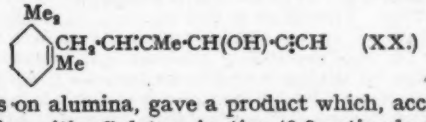


2370 A. ($\log \varepsilon = 4{\cdot}08$) and the presence of one active hydrogen atom, as indicated by a Zerewitinoff determination. We are now engaged on a study of the condensation of (XIV) with propargyl alcohol and analogues.

The possibility of preparing an ethinylcarbinol from the aldehyde (V) had also to be investigated. Ethinylcarbinols have been prepared from carbonyl compounds and acetylene in the presence of a variety of condensing agents such as sodamide, alkali-metal alkoxides or potassium hydroxide in ethereal solutions, or alkali metals or their amides in liquid ammonia. With substituted acetylenes, the Grignard method is often preferable, although not so convenient with acetylene itself owing to the difficulty of obtaining the pure monomagnesium bromide. There are but few references in the literature to the utilisation of unsaturated aldehydes in this type of condensation. Lespieau and Lombard (*Bull. Soc. chim.*, 1935, **2**, 369) and Teterin and Ivanov (*J. Gen. Chem. Russ.*, 1937, **7**, 1629) prepared ethinylcarbinols from crotonaldehyde and acraldehyde and their halogen substitution products in poor yield by the Grignard method and I.G. Farbenindustrie (B.P. 508,062) have condensed crotonaldehyde and acetylene under pressure in the presence of copper acetylide. Sodamide in liquid ammonia has been employed for the preparation of ethinylcarbinols from 1-methylacraldehyde and 2-ethylhexenal (Kreimeier, U.S.P. 2,106,181) and furfural (Macullum, U.S.P. 2,125,384).

Owing to the relative inaccessibility of (V) the condensation of citral with acetylene was examined in the first instance as a test case. 1-*Ethinylgeraniol* (XVIII) was prepared in 70% yield by reaction of the aldehyde with sodium acetylide (from sodium and not sodamide) in liquid ammonia and on treatment with acetic anhydride and pyridine at 100° readily yielded the *acetyl* derivative. Prolonged treatment of (XVIII) with

(XVIII.) $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH(OH){\cdot}C{:}CH$



(XX.)

(XIX.) $CMe_2{:}CH{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}C{:}CH$

acetic anhydride at 110°, followed by chromatographic analysis on alumina, gave a product which, according to its absorption spectrum (maximum at 2630 A.; $E^{1\%}_{1\,cm.}$ 900), a Zerewitinoff determination (0·9 active hydrogen atom), and a quantitative hydrogenation (4·6 molecules of hydrogen absorbed), consisted mainly of the hydrocarbon (XIX).

A similar condensation with the aldehyde (V) gave the ethinylcarbinol (XX) [6-(2′ : 6′ : 6′-*trimethylcyclohexenyl*)-4-*methylhex*-4-*en*-1-*yn*-2-*ol*], but, as was observed with 1-ethinylgeraniol, no solid derivatives could be obtained. The carbinol exhibited end absorption at 2190 A. ($\log \varepsilon = 4{\cdot}08$), similar to that of 1-ethinylgeraniol and consistent with its formulation as (XX). Acetylation with acetic anhydride and pyridine at 100° gave the *acetyl* derivative, which showed a maximum light absorption at 2370 A. ($\log \varepsilon = 4{\cdot}04$), indicating that this process is accompanied by a double bond migration resulting in the formation of a conjugated diene system. This isomerisation takes place to some extent in the carbinol itself, since with some specimens of (XX) absorption of low intensity ($E^{1\%}_{1\,cm.}$ 300—400) at 2300 A. has occasionally been observed.

Experimental.

The spectrographic data are for alcoholic solutions except that 2 : 4-dinitrophenylhydrazones were examined in chloroform.

β-Ionone.—The finely powdered semicarbazone (125 g., needles from 75% methyl alcohol, m. p. 142—144°), suspended in a mixture of light petroleum (500 c.c., b. p. 40—60°) and 2N-sulphuric acid (1200 c.c.), was shaken at 20° for 3 days (cf. Kon, J., 1930, 1616). After filtration the petroleum layer yielded β-ionone (79·5 g.), b. p. 82°/10^{-2} mm., $n_D^{19°}$ 1·5178. *Light absorption:* Maximum, 2930 A.; log ε = 4·11 (Ruzicka, Seidel, and Firmenich, *Helv. Chim. Acta*, 1941, **24**, 1434, give max. 2980 A.; log ε = 3·95. Burawoy, J., 1941, 20, gives max. 2935 A.; log ε = 3·94).

Condensation of β-Ionone with Ethyl Chloroacetate.—A solution of β-ionone (75 g., regenerated from the semicarbazone as above) and ethyl chloroacetate (96 g.) in light petroleum (150 c.c., b. p. 40—60°) was stirred vigorously in an atmosphere of nitrogen at − 60° while finely powdered sodium methoxide (36 g.) was added in small portions during 4 hours. The mixture, which had become orange-red and viscous, was stirred at − 60° for a further hour, and finally at 20° for 18 hours. After refluxing for 6 hours, the whole was cooled, treated with ice (200 g.), and acidified with 6N-acetic acid. The dark-coloured oil which separated was extracted with ether, and the extract washed with water and 2N-sodium bicarbonate. After drying and removal of solvent the residue was fractionally distilled, first at 20 mm. and finally at 0·2 mm., the portion (60 g.), b. p. 135—155°, $n_D^{21°}$ 1·5307, being retained. A middle cut from this fraction was twice distilled, yielding the *glycide* ester, b. p. 55° (bath temp.)/10^{-3} mm. (Found: C, 73·1; H, 9·15. $C_{17}H_{26}O_3$ requires C, 73·4; H, 9·35%). *Light absorption:* see Table I.

The Glycide Acid.—The ester (60 g.) was dissolved in alcoholic potassium hydroxide (250 c.c.; 10%) and kept at 20° for 24 hours. The mixture was diluted with water (1 l.) and, after the neutral portion had been removed with ether, the acid was liberated with 4N-phosphoric acid and isolated by means of ether as a red viscous oil (34 g.). The crude acid was treated with an equal volume of light petroleum (b. p. 40—60°) and kept at 0° over-night. The separated solid was washed with light petroleum (b. p. 40—60°) and on crystallisation from chloroform–light petroleum yielded the *glycide acid* (7·3 g.) in leaflets, m. p. 132° (decomp.), stable under nitrogen in the dark but rapidly becoming yellow and sticky on exposure to air and light. The acid is readily soluble in alcohol and methyl alcohol, hot chloroform and benzene and sparingly soluble in light petroleum (Found: C, 72·05; H, 8·8. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·85%). The *methyl* ester, prepared from the solid acid with diazomethane, had b. p. 70—80° (bath temp.)/10^{-4} mm., $n_D^{22°}$ 1·5540 (Found: C, 72·8; H, 8·9. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·1%).

Condensation of α-Ionone with Ethyl Chloroacetate.—A condensation with α-ionone (65 g.; $E^{1\%}_{1\,cm.}$ at 2265 A. = 610; $n_D^{25°}$ 1·4984), ethyl chloroacetate (83 g.), sodium methoxide (23 g.), and ether (100 c.c.) was carried out as described above. The resulting *glycide* ester (31·5 g.) had b. p. 135—145°/0·2 mm., 70° (bath temp.)/10^{-4} mm., $n_D^{24°}$ 1·4996 (Found: C, 73·4; H, 9·45. $C_{17}H_{26}O_3$ requires C, 73·4; H, 9·35%). The ester was hydrolysed as previously described but in this case the acid failed to crystallise.

Condensation of Mesityl Oxide with Ethyl Chloroacetate.—Starting from mesityl oxide (98 g.), ethyl chloroacetate (245 g.), sodium methoxide (108 g.), and ether (200 c.c.), the main reaction product (103 g.) had b. p 115—140°/20 mm., $n_D^{22°}$ 1·4624. On redistillation through a Widmer column the following fractions were collected: (1) B. p. 52—55°/1 mm. (31 g.), $n_D^{24°}$ 1·4552; (2) b. p. 58—63°/1 mm. (35 g.), $n_D^{24°}$ 1·4658; (3) b. p. 69—72°/1 mm. (18·5 g.), $n_D^{24°}$ 1·4661; (4) b. p. 80—90°/1 mm. (10 g.), $n_D^{24°}$ 1·4560. Redistillation of (1) indicated that it was not homogeneous and the upper fraction was consequently combined with (2) and refractionated: (2*a*) B. p. up to 58°/1 mm. (8 g.), $n_D^{22°}$ 1·4620; (2*b*) b. p. 59—61°/1 mm. (20 g.), $n_D^{24°}$ 1·4673. A middle cut from (2*b*) was redistilled, b. p. 60°/1 mm., $n_D^{24°}$ 1·4689 [Found: C, 63·6; H, 8·3. $C_9H_{14}O_3$ (Me ester) requires C, 63·5; H, 8·2%]. *Light absorption:* see Table II.

Fraction (3) was fractionated twice more; a middle cut had b. p. 65°/1 mm., $n_D^{24°}$ 1·4695 [Found: C, 64·5; H, 8·8. $C_{10}H_{16}O_3$ (Et ester) requires C, 65·2; H, 8·7%]. *Light absorption:* see Table II.

Hydrolysis of the mixed ester (20 g.) as described above gave a gum which partly crystallised in the presence of light petroleum (b. p. 40—60°) and a little chloroform. Recrystallisation of this solid (2·5 g.) from the same solvent mixture gave the *glycide acid* in needles, m. p. 72° (Found: C, 61·7; H, 7·6. $C_8H_{12}O_3$ requires C, 61·5; H, 7·7%). The methyl ester, prepared with diazomethane, had $n_D^{21°}$ 1·4791. *Light absorption:* see Table II.

3-(2′ : 6′ : 6′-*Trimethylcyclohexenyl*)-1-*methylcrotonaldehyde* (V).—The β-ionone glycide acid (crude, 65 g.) was treated with copper powder (0·2 g.) and heated in an oil-bath at 130°/15 mm. until decarboxylation appeared complete (about 1½ hours). The residue was distilled up to 180°/0·1 mm., and the distillate diluted with ether and dried. After removal of solvent the oil was fractionated through a Widmer column, yielding two fractions, (1) b. p. 80—90°/0·1 mm. (7 g.), which did not yield any ketonic derivatives, was inert towards sodium, and was not investigated further, and (2) b. p. 105—115°/0·1 mm. (14 g.), $n_D^{24°}$ 1·5059. *Thiosemicarbazone:* needles from methyl alcohol, m. p. 192° (Found: C, 64·5; H, 9·0; N, 14·75. $C_{15}H_{25}N_3S$ requires C, 64·5; H, 9·0; N, 15·05%). *Phenylsemicarbazone:* needles from methyl alcohol, m. p. 182° (Found: C, 74·5; H, 8·5; N, 12·4. $C_{21}H_{29}ON_3$ requires C, 74·3; H, 8·6; N, 12·4%). 2 : 4-*Dinitrophenylhydrazone:* red plates from alcohol, m. p. 164·5° (Found: C, 62·2; H, 6·7. $C_{20}H_{26}O_4N_4$ requires C, 62·0; H, 7·0%). The thiosemicarbazone (0·5 g.) and phthalic anhydride (3 g.) were steam-distilled for 20 hours in nitrogen; the oily distillate, after isolation by means of ether, yielded pure 3-(2′ : 6′ : 6′-*trimethylcyclohexenyl*)-1-*methylcrotonaldehyde* (0·4 g.), b. p. 45° (bath temp.)/10^{-4} mm., $n_D^{24°}$ 1·5067 (Found: C, 81·5; H, 10·95. $C_{14}H_{22}O$ requires C, 81·6; H, 10·7%). Treatment of this regenerated aldehyde with thiosemicarbazide gave the same derivative, m. p. 191—192° (mixed m. p.), as was obtained immediately from the decarboxylation.

3-(2′ : 6′ : 6′-*Trimethyl*-Δ$^{2'}$-cyclo*hexenyl*)-1-*methylcrotonaldehyde* (X).—The α-ionone glycide acid (18 g.) on decarboxylation by the method described above yielded an aldehyde (8·7 g.), b. p. 135—145°/0·3 mm., $n_D^{24°}$ 1·5016. *Thiosemicarbazone:* plates from aqueous methyl alcohol, m. p. 158—159° (Found: N, 14·9. $C_{15}H_{25}N_3S$ requires N, 15·05%). *Phenylsemicarbazone:* needles from aqueous methyl alcohol, m. p. 123—124° (Found: N, 12·3. $C_{21}H_{29}ON_3$ requires N, 12·4%). 2 : 4-*Dinitrophenylhydrazone:* red needles from methyl alcohol, m. p. 148·5—149·5° (Found: N, 14·35. $C_{20}H_{26}O_4N_4$ requires N, 14·5%). Regeneration of the aldehyde from the thiosemicarbazone yielded pure 3-(2′ : 6′ : 6′-*trimethyl*-Δ$^{2'}$-cyclo*hexenyl*)-1-*methylcrotonaldehyde*, b. p. 45° (bath temp.)/10^{-4} mm., $n_D^{24°}$ 1·5024 (Found: C, 81·6; H, 10·6. $C_{14}H_{22}O$ requires C, 81·6; H, 10·7%).

2 : 4-*Dimethylpentenals* (XII and XIII).—The glycide acid from mesityl oxide (crude, 40 g.) was heated with copper powder at 145°/760 mm. for ½ hour. The mixture of 2 : 4-dimethylpentenals (9·5 g.) obtained had b. p. 125—135°, $n_D^{24°}$ 1·4310, and no appreciable separation was observed on attempted fractionation. *Light absorption:* see Table III. Treatment of the aldehyde (1 g.) with semicarbazide acetate, followed by repeated crystallisation of the product from aqueous methyl alcohol, gave needles of the *semicarbazone* of 2 : 4-*dimethylpent-2-enal* (50 mg.), m. p. 184° (Found: C, 56·6; H, 8·95. $C_8H_{15}ON_3$ requires C, 56·8; H, 8·8%). *Light absorption:* Maximum, 2634 A.; log ε = 4·42. Regeneration of the aldehyde from the twice crystallised semicarbazone gave a product, containing a high proportion of the αβ-isomer, b. p. 130—135°, $n_D^{27°}$ 1·4355 (Found: C, 74·8; H, 10·65. $C_7H_{12}O$ requires C, 75·0; H, 10·7%). *Light absorption:* Maximum, 2270 A.; log ε = 3·94. The corresponding *phenylsemicarbazone* after repeated crystallisation from aqueous alcohol had m. p. about 125°, but after ten crystallisations from light petroleum (b. p. 40—60°) a small fraction was obtained in needles with the constant m. p. 178° (Found: C, 68·7; H, 7·9. $C_{14}H_{19}ON_3$ requires C, 68·6; H, 7·8%). The 2 : 4-*dinitrophenylhydrazone* was obtained in orange needles from alcohol, m. p. 164—165° (Found: N, 19·6. $C_{13}H_{16}O_4N_4$ requires N, 19·2%).

7-(2′ : 6′ : 6′-*Trimethyl*cyclo*hexenyl*)-5-*methylhepta*-3 : 5-*dien*-2-*one* (XIV).—A solution of the β-ionone C_{14} aldehyde (10 g., log ε at 2300 A. = 4·12) in a mixture of dry A.R. benzene (300 c.c.) and dry acetone (200 c.c.) was refluxed in an atmosphere of nitrogen for 48 hours together with freshly prepared aluminium *tert.*-butoxide (12 g.). The deep red suspension was treated with water and filtered, the benzene solution washed with water and dried, and the solvent removed under diminished pressure. Distillation of the residue from an electrically heated retort gave two fractions. (1) B. p. 60°/10^{-4} mm. (1·9 g.), $n_D^{20°}$ 1·5190. Unchanged aldehyde (phenylsemicarbazone, m. p. 182°). (2) B. p. 70—80°/10^{-4} mm. (4·2 g.), $n_D^{20°}$ 1·5420. *Light absorption:* Maximum, 2850 A.; log ε = 4·27. The *semicarbazone*, obtained in poor yield (2·0 g.), formed needles from methyl alcohol, m. p. 189—190° (decomp.), which varied with the rate of heating (Found: C, 71·2; H, 9·7; N, 14·1. $C_{18}H_{29}ON_3$ requires C, 71·25; H, 9·65; N, 13·9%). *Light absorption:* Maximum, 2930 A.; log ε = 4·67. Inflexion, 3040 A.; log ε = 4·62.

The finely powdered semicarbazone (2·3 g., m. p. 189—190°) was suspended in a mixture of light petroleum (100 c.c.; b. p. 40—60°) and 2N-sulphuric acid (40 c.c.) and heated under reflux for 48 hours with vigorous stirring. Working up in the usual manner gave 7-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-5-*methylhepta*-3 : 5-*dien*-2-*one* (0·8 g.) (0·9 g. of semicarbazone was recovered), as a pale yellow oil, b. p. 75—80° (bath temp.)/10^{-4} mm., $n_D^{19°}$ 1·5412 (Found: C, 82·8; H, 10·2. $C_{17}H_{26}O$ requires C, 82·9; H, 10·6%). This regenerated ketone gave the same semicarbazone, m. p. 189—190°, as did the crude material, indicating that the regeneration process has no adverse effect on the ketone.

8-(2′ : 6′ : 6′-*Trimethyl*cyclo*hexenyl*)-3 : 6-*dimethylocta*-4 : 6-*dien*-3-*ol* (XVII).—The C_{17} ketone described above (450 mg., $n_D^{25°}$ 1·5399, regenerated from the semicarbazone) was treated with ethylmagnesium bromide (from 100 mg. of magnesium) in ethereal solution. Decomposition of the Grignard complex with ammonium chloride and isolation of the product by means of ether yielded 8-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-3 : 6-*dimethylocta*-4 : 6-*dien*-3-*ol* (400 mg.) as a viscous oil, b. p. 70—80° (bath temp.)/10^{-4} mm., $n_D^{21°}$ 1·5003 (Found: C, 82·7; H, 11·8. $C_{19}H_{32}O$ requires C, 82·5; H, 11·7%). The carbinol (143 mg.) gave 12 c.c. of methane at 19°/758 mm. equivalent to 1·0 active hydrogen atom per molecule.

1-*Ethinylgeraniol* (XVIII).—Purified dry acetylene was rapidly passed into a stirred solution of sodium (18 g.) in liquid ammonia (1000 c.c.) until the solution became colourless. A solution of citral (100 g.) in dry ether (400 c.c.) was then added during ½ hour and stirring and cooling were continued for a further 3 hours. After standing overnight the residue was decomposed with dilute hydrochloric acid (ice), and the ethereal layer washed, dried, and evaporated. Distillation of the product through a Widmer column gave 1-*ethinylgeraniol* (80 g.) as a colourless oil, b. p. 88°/0·02 mm., $n_D^{20°}$ 1·4875 (Found: C, 80·9; H, 10·9. $C_{12}H_{18}O$ requires C, 80·85; H, 10·2%). The carbinol (140 mg.) evolved 34·7 c.c. of methane at 767 mm./19° (after heating to 90°), equivalent to 1·9 active hydrogen atoms per molecule. The carbinol yielded insoluble silver and mercury salts and its ultra-violet absorption spectrum showed only end absorption (at 2150 A.; $E^{1\%}_{1\,cm.}$ = 250). A mixture of the carbinol (27·5 g.), acetic anhydride (34 g.), and pyridine (27·5 g.) was heated at 100° for an hour in nitrogen. After removal of the reagents the *acetyl* derivative (26·5 g.) was obtained, b. p. 92—95°/0·5 mm., $n_D^{22°}$ 1·4728 (Found: C, 76·5; H, 9·0; OAc, 19·4. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·1; OAc, 19·5%). The acetate (4·00 mg.) evolved 0·376 c.c. of methane at 24°/771 mm. (after heating to 90°), equivalent to 0·9 active hydrogen atom per molecule. The ultra-violet absorption spectrum was similar to that of the carbinol.

6-(2′ : 6′ : 6′-*Trimethyl*cyclo*hexenyl*)-4-*methylhex*-4-*en*-1-*yn*-2-*ol* (XX).—Prepared by a similar method as for 1-ethinylgeraniol from the β-ionone C_{14} aldehyde (16 g.), the *carbinol* (6 g.) had b. p. 115—120°/10^{-3} mm., $n_D^{22°}$ 1·5165 (Found: C, 83·1; H, 10·2. $C_{16}H_{24}O$ requires C, 82·8; H, 10·35%). It (7·70 mg.) evolved 0·14 c.c. of methane at 25°/771 mm. (after heating to 90°), equivalent to 1·8 active hydrogen atoms per molecule. The *acetyl* derivative, prepared by the method used with 1-ethinylgeraniol, had b. p. 130—135°/0·1 mm., $n_D^{21·5°}$ 1·5135 (Found: C, 78·6; H, 9·8. $C_{18}H_{26}O_2$ requires C, 78·8; H, 9·5%). It (6·65 mg.) evolved 0·52 c.c. of methane at 22°/761 mm. (after heating to 90°), equivalent to 0·9 active hydrogen atom per molecule.

The authors are indebted to the Rockefeller Foundation and also to I.C.I. (Dyestuffs) Ltd. for financial assistance which rendered this work possible.

Imperial College of Science and Technology, London, S.W. 7. [*Received, September 21st*, 1942.]

158. *Studies in the Polyene Series. Part VI. The Preparation of Ethinylcarbinols from αβ-Unsaturated Aldehydes.*

By E. R. H. Jones and J. T. McCombie.

αβ-Unsaturated aldehydes are readily converted into ethinylcarbinols by reaction with sodium acetylide in liquid ammonia, a method which, when applied to benzaldehyde, gives an 82·5% yield of phenylethinylcarbinol. The aldehydes now studied include crotonaldehyde (60% yield of carbinol), acraldehyde (35%), 2-methylcrotonaldehyde (50%), tiglic aldehyde (75%), 2-ethylhex-2-enal (80%), furfuraldehyde (65%), and cinnamaldehyde (2%). The carbinols have been characterised by the preparation of crystalline derivatives, particularly the *naphthylurethanes*, and also by complete hydrogenation to the known saturated secondary alcohols.

In view of current general interest in acetylenic carbinols and more particularly because of their potential importance for the synthesis of vitamin A and analogues (see preceding paper) a detailed investigation of the preparation and properties of the acetylenic carbinols derived from αβ-unsaturated aldehydes has been initiated. This paper deals with the preparation and characterisation of the ethinylcarbinols of certain αβ-unsaturated aldehydes (the literature is surveyed in the preceding paper). Accounts of their interesting reactions and also of investigations which are being made with other types of acetylenic carbinols formed from unsaturated aldehydes, and also with ethinylcarbinols from polyene aldehydes, will appear in subsequent publications in this series.

The method involves the preparation of sodium acetylide (from sodium) in liquid ammonia solution, followed by addition of the appropriate aldehyde, usually in ethereal solution, acetylene being passed into the reaction mixture throughout the whole time of reaction (cf. Campbell, Campbell, and Eby, *J. Amer. Chem. Soc.*, 1938, **60**, 2882). The sodium acetylide was prepared according to Vogt's method (U.S.P.

2,200,941), whereby no appreciable dissolved excess of sodium is ever present in the solution. When the above procedure was employed with benzaldehyde, an 82·5% yield of phenylethinylcarbinol was achieved (Campbell, Campbell, and Eby, *loc. cit.*, obtained only a 45% yield), and in order to investigate the formation of crystalline derivatives from these ethinylcarbinols the *phenylurethane*, p-*nitrophenylurethane*, β-*naphthylurethane*, and the *acid phthalate* were prepared.

Propenylethinylcarbinol was readily obtained from crotonaldehyde in 50—65% yields and was characterised by its *phenylurethane*, β-*naphthylurethane*, and *acetyl* derivative. Complete hydrogenation in the presence of palladium–norit yielded ethylpropylcarbinol (*phenylurethane*), which was oxidised to ethyl propyl ketone. Acraldehyde yielded vinylethinylcarbinol in only 36% yield, however, much solid polymeric material being formed under all conditions of experiment. This carbinol was characterised by the formation of a *phenylurethane* and an α-*naphthylurethane* and gave diethylcarbinol on complete hydrogenation. A 50% yield of iso*butenylethinylcarbinol* (*phenylurethane*, β-*naphthylurethane*) was obtained from 2-methylcrotonaldehyde, the constitution of the carbinol being proved by its complete hydrogenation to ethyl*iso*butylcarbinol (also oxidised to ethyl *iso*butyl ketone). 2-Ethylhex-2-enal gave the ethinylcarbinol (4-ethyloct-4-en-1-yn-3-ol) (α-*naphthylurethane*) in 85% yield (Kreimeier, U.S.P. 2,106,181, obtained the carbinol in 56% yield). From tiglic aldehyde a 75% yield of 4-*methylhex*-4-*en*-1-*yn*-3-*ol* (α-*naphthylurethane*) was obtained. 2-Furylethinylcarbinol was produced in 65% yield from furfuraldehyde (Macullum, U.S.P. 2,125,384, mentions a 30% yield), but from cinnamaldehyde only a 2% yield of *styrylethinylcarbinol* could be obtained, a large quantity of a solid polymer being simultaneously produced.

When the above ethinylcarbinols react with methylmagnesium iodide in Zerewitinoff determinations the temperature has to be raised to 90° before reaction with the acetylenic hydrogen atom is complete. The preferential reaction with the active hydrogen atom of the hydroxyl group is proved by the fact that the acetate of propenylethinylcarbinol gave practically no methane at 20°.

Experimental.

Absorption spectra were determined in alcoholic solutions. All distillations were carried out in a nitrogen atmosphere. Except where stated otherwise, light petroleum refers to that fraction of b. p. 40—60°.

Phenylethinylcarbinol.—Purified acetylene was rapidly passed into liquid ammonia (1000 c.c.) with stirring and cooling, and sodium (23 g.) added in small pieces in such a manner that the blue colour never persisted for more than a few moments. A solution of benzaldehyde (106 g.) in ether (100 c.c.) was then added during an hour, and the mixture stirred and cooled for a further 3 hours with continued introduction of acetylene. The ammonia was allowed to evaporate overnight and ether and dilute sulphuric acid (ice) were added to the residue. Isolation of the product in the usual manner gave phenylethinylcarbinol (110 g.), as prisms, m. p. 22°, b. p. 115—116°/16 mm., $n_D^{21°}$ 1·5482 (Campbell, Campbell, and Eby, *loc. cit.*, gave b. p. 114°/12 mm., $n_D^{20°}$ 1·5508). *Active hydrogen* (Zerewitinoff): The carbinol (130 mg.) gave 44·5 c.c. of methane at 22°/761 mm. (after heating to 85°), equivalent to 1·9 active hydrogen atoms per molecule. *Phenylurethane:* Equimolecular quantities of the carbinol and phenyl *iso*cyanate were set aside at 20° for several days in a sealed tube. The crystalline mass was washed with light petroleum and two crystallisations of the residue from light petroleum (b. p. 60—80°) gave the *phenylurethane* in needles, m. p. 81—82° (Found: N, 5·55. $C_{16}H_{13}O_2N$ requires N, 5·55%). p-*Nitrophenylurethane:* The reagents were heated together in dry xylene for an hour, the dinitrophenylurea removed, and after standing at 0° for several days the derivative separated. Recrystallisation from xylene gave the p-*nitrophenylurethane* in pale yellow needles, m. p. 132° (Found: N, 9·0. $C_{16}H_{12}O_4N_2$ requires N, 8·95%). β-*Naphthylurethane:* The mixed reagents were heated for an hour at 100° and after standing overnight at 20° the crude product was extracted with boiling petroleum (b. p. 100—120°); on cooling and after recrystallisation from the same solvent the β-*naphthylurethane* was obtained in needles, m. p. 120° (Found: N, 4·55. $C_{20}H_{15}O_2N$ requires N, 4·65%). *Acid phthalate:* Equimolecular quantities of the carbinol and phthalic anhydride were heated in pyridine solution at 100° for 2 hours and the derivative, removed from ethereal solution with N-ammonia, was isolated by means of chloroform. The crude product was purified both by adsorption on alumina from benzene solution, and by extraction with hot light petroleum (b. p. 60—80°); crystallisation from the latter solvent gave the *acid phthalate* in needles, m. p. 98—99° (Found: C, 73·1; H, 4·7. $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%). The *acetyl* derivative, prepared by heating the carbinol with acetic anhydride at 100—115° for 2½ hours, had b. p. 124°/18 mm., $n_D^{20°}$ 1·5155 (Found: C, 76·2; H, 6·05. $C_{11}H_{10}O_2$ requires C, 75·9; H, 5·8%). The mercury compound separated from alcohol in aggregates of needles, m. p. 167—168°.

Propenylethinylcarbinol.—To sodium acetylide, prepared from sodium (230 g.) as above, in liquid ammonia (6000 c.c.) in a 10-litre 3-necked flask, crotonaldehyde (700 g.) was added during 2 hours with stirring and cooling. After the addition of ammonium chloride (525 g.) the ammonia was allowed to evaporate overnight; water and ice (1 kg.) were then added, and the carbinol distilled in steam. The steam-distillate was saturated with salt and after isolation with ether and distillation through a Widmer column propenylethinylcarbinol (565 g.) (in experiments on a somewhat smaller scale, yields up to 65% were obtained) was obtained as a colourless oil, b. p. 154—156°, 102—103°/111 mm., 75°/24 mm., $n_D^{23°}$ 1·4651 (Lespieau and Lombard, *Bull. Soc. chim.*, 1935, **2**, 369, give b. p. 153°, 58—59°/13 mm., $n_D^{23°}$ 1·4650) (Found: C, 75·1; H, 8·0. Calc. for C_6H_8O: C, 75·0; H, 8·4%). The carbinol gives white silver and mercury compounds, the latter forming small prisms, m. p. above 360°. It exhibits no absorption in the ultra-violet with $E_{1\,cm.}^{1\%}$ greater than 35, between 2150—5000 A. *Active hydrogen* (Zerewitinoff): The carbinol (99·2 mg.) evolved 27·2 c.c. of methane at 20°/773 mm., after heating to 90°, equivalent to 1·9 active hydrogen atoms per molecule. *Phenylurethane:* After standing at 20° for 14 days, the reaction mixture crystallised at 0° and formed needles from light petroleum, m. p. 65° (Found: N, 6·55. $C_{13}H_{13}O_2N$ requires N, 6·5%). The β-*naphthylurethane*, prepared as described above, crystallised in needles, m. p. 89°, from light petroleum or aqueous methyl alcohol (Found: N, 5·3. $C_{17}H_{15}O_2N$ requires N, 5·3%). *Acetyl derivative:* A mixture of propenylethinylcarbinol (96 g.) and acetic anhydride (120 g.) was heated at 110° for 4 hours. Isolation in the usual manner yielded the *acetyl* derivative (111·5 g.), b. p. 110—112°/100 mm., $n_D^{20·5°}$ 1·4463 (Found: C, 69·8; H, 7·2. $C_8H_{10}O_2$ requires C, 69·6; H, 7·25%). This compound exhibits practically no absorption in the 2150—5000 A. range. *Active hydrogen* (Zerewitinoff): The acetate (157 mg.) gave 29·1 c.c. of methane at 19·5°/766 mm., after heating to 90°, corresponding to 1·1 active hydrogen atoms per molecule.

Ethylpropylcarbinol.—A solution of propenylethinylcarbinol (5 g.) in methyl alcohol (50 c.c.) was shaken with hydrogen in the presence of palladium–norit (1·5 g.; 10%) until absorption was complete. The catalyst was filtered

off, and the solvent removed through a column; the residual ethylpropylcarbinol had b. p. 134—136° (Völker, *Ber.*, 1875, **8**, 1019, gives b. p. 135°). A synthetic specimen of this alcohol made by treating ethylmagnesium bromide with butaldehyde had b. p. 135—136°, the *phenylurethane* of either specimen crystallised from light petroleum in needles, m. p. 49—50°, and no depression was observed on admixture (Found: N, 6·4. $C_{12}H_{19}O_2N$ requires N, 6·35%). A small portion of each specimen of the alcohol was oxidised to the ketone with chromic anhydride in dilute sulphuric acid. No depressions in m. p. were observed on admixture of the 2 : 4-dinitrophenylhydrazones, m. p. 134—135° (purified by adsorption on alumina) (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2958, gives m. p. 130°) or the semicarbazones, m. p. 112° (Pickard and Kenyon, J., 1913, **103**, 1942, give m. p. 112°) of the two ketones.

Vinylethinylcarbinol.—The crude condensation product from acraldehyde (58 g.) and sodium (25 g.) yielded amorphous polymeric material (40 g.). This was washed with ether and the aqueous solution, after saturation with salt, was thoroughly extracted. The combined ethereal extracts were washed with saturated brine and sodium bicarbonate solution, dried, and evaporated. Two distillations of the residual liquid gave vinylethinylcarbinol (30 g.), b. p. 83·5—84·5°/150 mm. (Lespieau and Lombard, *loc. cit.*, give b. p. 128·5—129·5°), $n_D^{16°}$ 1·4545. The carbinol is appreciably soluble in water and gives white silver and mercury compounds. It exhibits practically no absorption in the range 2150—5000 A. *Active hydrogen* (Zerewitinoff): Vinylethinylcarbinol (61 mg.) gave 37·5 c.c. of methane at 23°/768 mm., after heating to 90°, corresponding to 2·1 active hydrogen atoms per molecule. The *phenylurethane* formed needles, m. p. 37°, from light petroleum (Found: N, 7·1. $C_{13}H_{11}O_2N$ requires N, 6·95%). The *α-naphthylurethane* was obtained in needles, m. p. 127·5—128·5°, from light petroleum (Found: N, 5·45. $C_{14}H_{13}O_2N$ requires N, 5·6%). The carbinol (3·4 g.) was refluxed with acetic anhydride (5 g.) for 15 hours and isolation in the usual manner gave the *acetate* (4 g.), b. p. 87—88°/100 mm., $n_D^{23°}$ 1·4319 (Found: C, 67·6; H, 6·7. $C_7H_8O_2$ requires C, 67·75; H, 6·45%). This derivative shows no appreciable absorption in the range 2150—5000 A.

Diethylcarbinol.—Vinylethinylcarbinol (3 g.) in ether (150 c.c.) was shaken with platinic oxide (0·1 g.) and hydrogen until absorption ceased. The catalyst was separated, and the ether distilled through a column; the residual diethylcarbinol had b. p. 114—116°, $n_D^{18°}$ 1·4071 (Rosanow, *Chem. Zentr.*, 1923, I, 1490, gives b. p. 116·2°, $n_D^{20°}$ 1·4057). The α-naphthylurethane had m. p. 90—91° (Bicket and French, *J. Amer. Chem. Soc.*, 1926, **48**, 747, give m. p. 71—72°, presumably a misprint), and the 3 : 5-dinitrobenzoate had m. p. 98—99° (Conant and Blatt, *ibid.*, 1929, **51**, 1227, give m. p. 101°). No depressions were observed on admixture with authentic specimens.

iso*Butenylethinylcarbinol.*—Prepared by the standard method from 2-methylcrotonaldehyde (26 g.) and sodium (7·1 g.), iso*butenylethinylcarbinol* (17 g.) was obtained, b. p. 110—113°/100 mm., $n_D^{20°}$ 1·4657 (Found: C, 76·2; H, 9·2. $C_7H_{10}O$ requires C, 76·35; H, 9·1%). It exhibits no appreciable light absorption in the 2150—5000 A. range. The *phenylurethane*, prepared in the manner already described, crystallised in leaflets, m. p. 58—59°, from light petroleum (Found: C, 73·6; H, 6·7. $C_{14}H_{15}O_2N$ requires C, 73·35; H, 6·55%). The *β-naphthylurethane* formed leaflets, m. p. 76°, from light petroleum (Found: C, 77·85; H, 6·6. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1%).

*Ethyl*iso*butylcarbinol.*—A solution of *iso*butenylethinylcarbinol (8·5 g.) in acetic acid (80 c.c.) was shaken with hydrogen and platinic oxide (0·1 g.). When absorption was complete the catalyst was removed, and the filtrate neutralised with sodium hydroxide solution and extracted with ether. The ethyl*iso*butylcarbinol isolated had b. p. 93—96°/105 mm., $n_D^{20°}$ 1·4128 (Wagner, *Bull. Soc. chim.*, 1884, **42**, 330, gives b. p. 147—148°). The α-naphthylurethane had m. p. 72—73° (Levene and Walti, *J. Biol. Chem.*, 1931, **94**, 367, give m. p. 74—75°). Oxidation with chromic anhydride in dilute sulphuric acid yielded ethyl *iso*butyl ketone, which gave a semicarbazone, m. p. 150° (Rhinesmith, *J. Amer. Chem. Soc.*, 1936, **58**, 596, gives m. p. 149—150°), and a 2 : 4-dinitrophenylhydrazone, m. p. 73° (Allen, *ibid.*, 1930, **52**, 2955, gives m. p. 75°).

4-*Ethyloct*-4-*en*-1-*yn*-3-*ol.*—Prepared by the standard method from 2-ethylhex-2-enal (86 g.) and sodium (15·7 g.), 4-ethyloct-4-en-1-yn-3-ol (88 g.) was obtained, b. p. 96·5—97°/14 mm., $n_D^{20°}$ 1·4678 (Kreimeier, *loc. cit.*, records b. p. 115—115·5°/34 mm.). The carbinol exhibits no appreciable light absorption in the 2150—5000 A. range. The *α-naphthylurethane* formed needles, m. p. 57—58°, from light petroleum (Found: N, 4·4. $C_{21}H_{23}O_2N$ requires N, 4·35%).

4-*Methylhex*-4-*en*-1-*yn*-3-*ol.*—Condensation of tiglic aldehyde (54 g.) with sodium acetylide (from 15 g. of sodium) in liquid ammonia in the usual manner gave 4-*methylhex*-4-*en*-1-*yn*-3-*ol* (55 g.), b. p. 96—97°/50 mm., $n_D^{24°}$ 1·4673 (Found: C, 76·2; H, 9·2. $C_7H_{10}O$ requires C, 76·35; H, 9·1%). The carbinol shows no appreciable absorption in the range 2150—5000 A. The *α-naphthylurethane* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 105° (Found: C, 77·45; H, 6·2. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1%).

2-*Furylethinylcarbinol.*—Prepared by the standard procedure from furfuraldehyde (96 g.) and sodium (23 g.), 2-furylethinylcarbinol (79 g.) was obtained as an almost colourless oil, b. p. 83—85°/2 mm. (Macullum, *loc. cit.*, gives b. p. 100—103°/25 mm.). The carbinol is fairly sensitive to oxidation and slowly darkens even in a nitrogen atmosphere. *Active hydrogen* (Zerewitinoff): The carbinol (104 mg.) gave 36·5 c.c. of methane at 20·5°/762 mm., after heating to 90°, equivalent to 1·9 active hydrogen atoms per molecule.

Styrylethinylcarbinol.—When cinnamaldehyde (132 g.) was condensed with sodium acetylide (from sodium, 23 g.) in the normal manner, the crude product contained polymeric material (more than 100 g.), insoluble in ether. The ether-soluble portion of the product was distilled, yielding an oil (3 g.), b. p. 130—140°/12 mm., which crystallised on cooling, yielding *styrylethinylcarbinol* in needles, m. p. 66—67°, from light petroleum (Found: C, 83·6; H, 6·5. $C_{11}H_{10}O$ requires C, 83·5; H, 6·3%). *Light absorption:* Maximum, 2510 A.; log ε = 4·31.

The authors are indebted to Professor I. M. Heilbron, D.S.O., F.R.S., for his interest in this work and to the Rockefeller Foundation and I.C.I. (Dyestuffs) Ltd. for grants.

Imperial College of Science and Technology, London, S.W. 7. [*Received, September 21st*, 1942.]

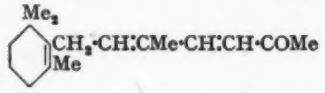
---

159. *Studies in the Polyene Series. Part VII. Carbinols from Propargyl Acetal.*

By I. M. Heilbron, E. R. H. Jones, and H. P. Koch.

Carbinols have been prepared by the Grignard reaction of propargyl acetal with propaldehyde, methyl ethyl ketone, and benzyl methyl ketone and these have been characterised as the *urethane* derivatives. A facile cyclisation ensues on semihydrogenation of the acetylenic bond resulting in the formation of dihydrofuran derivatives.

In Part V (this vol., p. 727) a scheme for the synthesis of an analogue of vitamin A, dependent upon the condensation of the C_{17} ketone (I) with propargyl derivatives, was outlined. It has already been demonstrated that the ketone (I) reacts normally with ethylmagnesium bromide and experiments are now described to determine the possibility of employing propargyl acetal (II) (Grard, *Ann. chim.*, 1930, **13**, 336) as the second component in the projected synthesis.

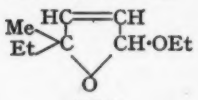
(I.) 

$CH{\equiv}C{\cdot}CH(OEt)_2$ (II.)

$CR_1R_2(OH){\cdot}C{\equiv}C{\cdot}CH(OEt)_2$ (III.)

Condensation of propargylacetalmagnesium bromide (Grard, *loc. cit.*) with propaldehyde, methyl ethyl ketone, and benzyl methyl ketone gave approximately 40% yields of 6 : 6-*diethoxyhex*-4-*yn*-3-*ol* (III; $R_1 = H$, $R_2 = Et$), 6 : 6-*diethoxy*-3-*methylhex*-4-*yn*-3-*ol* (III; $R_1 = Me$, $R_2 = Et$), and 5 : 5-*diethoxy*-1-*phenyl*-2-*methylpent*-3-*yn*-2-*ol* (III; $R_1 = Me$, $R_2 = CH_2Ph$) respectively. As none of these carbinols gave consistent results in carbon and hydrogen determinations, they were characterised as the *urethane* derivatives [$-CH(NH{\cdot}CO_2Et)_2$] (m. p.'s 143°, 111°, and 130° respectively) by reaction with urethane in the presence of dilute hydrochloric acid, and furthermore they all evolved approximately one molar volume of methane in Zerewitinoff determinations. Unlike acetals of αβ-ethylenic aldehydes, these acetals and also propargyl acetal itself, fail to give 2 : 4-dinitrophenylhydrazones on treatment with a warm solution of the hydrazine hydrochloride in alcohol. Attempts directly to dehydrate the carbinols (III) to the vinylacetylene acetals resulted either in extensive decomposition or in the recovery of unchanged material.

Small-scale quantitative hydrogenation experiments with the three carbinols, a palladium–calcium carbonate catalyst being used, revealed a very marked decrease in the hydrogenation velocity after approximately one molar volume of hydrogen had been absorbed. When 6 : 6-diethoxy-3-methylhex-4-yn-3-ol (III; $R_1 = Me$, $R_2 = Et$) was semihydrogenated in methyl alcohol on a moderate scale, however, a complex mixture was obtained, which was partially resolved into its components on careful fractionation with an efficient column. The isolation of ethyl alcohol indicated that the primary semihydrogenation product had undergone cyclisation and the product of this facile ring closure, a substance to which the constitution 2-*ethoxy*-5-*methyl*-5-*ethyl*-Δ^3-*dihydrofuran* (IV), is ascribed, was isolated in small yield. In support of this formulation are the facts that this product evolved no methane in a Zerewitinoff estimation, exhibited no absorption in the ultra-violet, and failed to form a urethane derivative. It readily decolorised a solution of bromine in carbon tetrachloride and, like the 2-ethoxy-5-methyltetrahydrofuran described by Helferich (*Ber.*, 1919, **52**, 1123), was found to be stable to cold dilute hydrochloric acid. With a hot alcoholic solution of 2 : 4-dinitrophenylhydrazine hydrochloride the 2 : 4-*dinitrophenylhydrazone* of 3-*methylsorbic aldehyde* (V) is produced by simultaneous hydrolysis and dehydration, its constitution being indicated by analytical data and its absorption spectrum, characteristic of that of a dinitrophenylhydrazone of a doubly unsaturated



(IV.)

(V.) $CH_3{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CHO$ $CH_3{\cdot}CH_2{\cdot}C(OH)Me{\cdot}CH{:}CH{\cdot}CHO$ (VI.)

aldehyde. With warm semicarbazide acetate a small yield of a *derivative*, m. p. 169°, is formed, the analytical data for which agree with that of the semicarbazone of the undehydrated aldehyde, 4-hydroxy-4-methylhex-2-enal (VI).

Semihydrogenation of 5 : 5-diethoxy-1-phenyl-2-methylpent-3-yn-2-ol (III; $R_1 = Me$, $R_2 = CH_2Ph$) similarly gave a poor yield of a dihydrofuran and since these hemiacetals are not readily convertible into the required unsaturated aldehydes this investigation has been abandoned in favour of more promising routes employing other propargyl derivatives.

Experimental.

6 : 6-*Diethoxyhex*-4-*yn*-3-*ol*.—An ethereal solution of ethylmagnesium bromide (from 3·8 g. of magnesium) was slowly added with stirring and cooling to propargyl acetal (20 g.) (Grard, *loc. cit.*) in ether (200 c.c.). After 2 hours a solution of propaldehyde (9 g.) in ether (50 c.c.) was dropped into the mixture, which was stirred overnight at 20°. Decomposition of the Grignard complex was effected with ammonium chloride and after recovery of unchanged propargyl acetal (7 g.), b. p. 35—42°/13 mm., 6 : 6-*diethoxyhex*-4-*yn*-3-*ol* (12 g.), b. p. 107°/3 mm., $n_D^{18°}$ 1·4476, was isolated. Carbon and hydrogen determinations with this and other acetylenic acetals gave inconsistent results. *Active hydrogen* (Zerewitinoff): The carbinol (158 mg.) evolved 18·6 c.c. of methane at 24°/773 mm., equivalent to 0·9 active hydrogen atom per molecule. *Urethane derivative*: The carbinol (300 mg.) was shaken for 2 hours with a solution of urethane (1 g.) in N-hydrochloric acid (10 c.c.). The white precipitate formed was crystallised from aqueous methyl alcohol, yielding the *urethane* derivative as a microcrystalline powder, m. p. 143° (Found: N, 10·1. $C_{13}H_{20}O_5N_2$ requires N, 10·3%).

6 : 6-*Diethoxy*-3-*methylhex*-4-*yn*-3-*ol*.—When the above condensation was carried out with methyl ethyl ketone (11·3 g.), 6 : 6-*diethoxy*-3-*methylhex*-4-*yn*-3-*ol* (11·5 g.), b. p. 88°/3 mm., $n_D^{21°}$ 1·4444, was obtained. *Active hydrogen* (Zerewitinoff): The carbinol (179 mg.) evolved 24·7 c.c. of methane at 31°/764 mm., equivalent to 1·1 active hydrogen atoms per molecule. The *urethane* derivative, prepared as previously described, separated from petroleum (b. p. 100—120°) as a powder, m. p. 111° (Found: N, 9·4. $C_{13}H_{22}O_5N_2$ requires N, 9·8%).

5 : 5-*Diethoxy*-1-*phenyl*-2-*methylpent*-3-*yn*-2-*ol*.—Employment of benzyl methyl ketone (21 g.) in the above condensation gave as main product 5 : 5-*diethoxy*-1-*phenyl*-2-*methylpent*-3-*yn*-2-*ol* (18·7 g.), b. p. 128°/3 mm., $n_D^{22°}$ 1·5032. *Active hydrogen* (Zerewitinoff): The carbinol (232 mg.) evolved 20·9 c.c. of methane at 23°/767 mm., equivalent to 1·0 active hydrogen atom per molecule. The *urethane* derivative separated from petroleum (b. p. 100—120°) as a powder m. p. 130° (Found: N, 8·2. $C_{18}H_{24}O_5N_2$ requires N, 8·1%).

Semihydrogenation of 6 : 6-*Diethoxy*-3-*methylhex*-4-*yn*-3-*ol.*—A solution of the carbinol (24·7 g.) in methyl alcohol (200 c.c.; free from ethyl alcohol) was shaken with hydrogen in the presence of palladium–calcium carbonate (4 g.; 2%), one molar volume of hydrogen (2750 c.c.) being absorbed rapidly. The hydrogenation was then interrupted, the catalyst removed, and the solution distilled through a well-lagged column packed with single-turn glass helices, fitted with a total condensation-variable take off head and operating at a reflux ratio of about 10 : 1. The following main fractions were collected : (i) B. p. 65°, methyl alcohol. (ii) B. p. 35—36°/100 mm. (2 g.), ethyl alcohol (identified as the 3 : 5-dinitrobenzoate, m. p. 92°). (iii) B. p. 74—82°/50 mm. (4·4 g.). (iv) B. p. 98—114°/4 mm. (8 g.).

On redistillation, fraction (iii) gave 2-*ethoxy*-5-*methyl*-5-*ethyl*-Δ^2-*dihydrofuran* as a colourless oil with a strong camphoraceous odour, b. p. 151°, 76°/50 mm., 46°/19 mm., $n_D^{20°}$ 1·4268 (Found : OEt, 29·2. $C_7H_{11}O{\cdot}OEt$ requires OEt, 28·9%). On boiling with 2 : 4-dinitrophenylhydrazine in alcoholic hydrochloric acid solution a red precipitate was obtained. Purification by adsorption on alumina from benzene solution and crystallisation from alcohol gave the 2 : 4-*dinitrophenylhydrazone* of 3-*methylsorbic aldehyde* in red needles, m. p. 194° (Found : C, 54·0; H, 4·8; N, 19·1. $C_{13}H_{14}O_4N_4$ requires C, 53·8; H, 4·8; N, 19·3%). *Light absorption in alcohol :* Maximum, 3910 A.; log $\epsilon = 4{\cdot}56$. With semicarbazide acetate in hot water, fraction (iii) gave a small yield of a solid which separated from water as a powder, m. p. 169° (Found : C, 52·3; H, 8·2. $C_8H_{15}O_2N_3$ requires C, 51·9; H, 8·1%). *Light absorption in alcohol :* Maximum, 2680 A.; log $\epsilon = 4{\cdot}58$. These analytical and spectrographic data suggest that the substance is the *semicarbazone* of 4-*hydroxy*-4-*methylhex*-2-*enal.*

On redistillation, fraction (iv) had b. p. 110°/4 mm., $n_D^{19°}$ 1·4565. It gave no methane in a Zerewitinoff determination and exhibited no ultra-violet absorption (Found : OEt, 17·5. $C_{14}H_{21}O_2{\cdot}OEt$ requires OEt, 16·9%).

The authors are indebted to the Rockefeller Foundation for financial assistance and to the University of London for the award of a Postgraduate Studentship.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7. [*Received, September 21st*, 1942.]

---

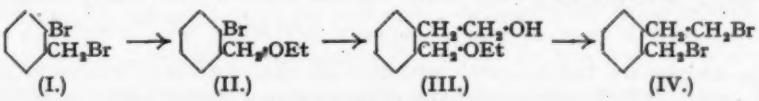
160. *The Synthetic Application of* o-β-*Bromoethylbenzyl Bromide. Part I. Sulphanilamide Derivatives of* 1 : 2 : 3 : 4-*Tetrahydroisoquinoline.*

By FREDERICK G. HOLLIMAN and FREDERICK G. MANN.

A method for preparing *o*-β-bromoethylbenzyl bromide readily in good yield is described. A number of sulphanilamide derivatives containing the 2-(1 : 2 : 3 : 4-tetrahydro*iso*quinolyl) group, and also certain sulphanilic hydrazide derivatives, have been prepared and their bactericidal properties determined.

o-β-BROMOETHYLBENZYL bromide (IV) has obviously great synthetic value for the preparation of *N*-substituted 1 : 2 : 3 : 4-tetrahydro*iso*quinolines and of related compounds in which the nitrogen is replaced by other elements. Its past use has been severely limited, however, by its laborious preparation. Von Braun and Zobel (*Ber.*, 1923, **56**, 2142) have described a synthesis of the bromide from *o*-toluidine which involves eleven stages : if the highest yield by modern methods for the conversion of *o*-toluidine into *o*-cyanobenzyl bromide is taken (65%), and von Braun and Zobel's optimum yields for the remaining nine stages then considered, the over-all yield of the *o*-β-bromoethylbenzyl bromide from *o*-toluidine is 3·5% of the theoretical. The practical value of this synthesis is clearly very small.

We have worked out a synthesis from *o*-toluidine which involves five stages and gives an over-all yield of 8%. *o*-Toluidine is converted into *o*-bromotoluene and the latter into *o*-bromobenzyl bromide (I) by the method of Kenner and Wilson (J., 1927, 1110). Treatment with sodium ethoxide gives o-*bromobenzyl ethyl ether* (II). The conversion of the latter into a Grignard reagent at first gave great difficulty : ultimately, by



(I.) (II.) (III.) (IV.)

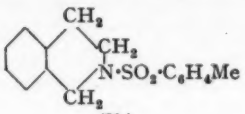
using specially activated magnesium and diluting the bromo-ether (II) with ethyl bromide (Grignard's "entrainment method," *Compt. rend.*, 1934, **198**, 625), the reagent was satisfactorily prepared, and when treated with ethylene oxide gave *o*-β-hydroxyethylbenzyl ethyl ether (III), the penultimate stage in von Braun and Zobel's synthesis. These authors converted this ether (III) into *o*-β-bromoethylbenzyl bromide (IV) by the action of hydrobromic acid, purifying the final product by distillation : we find that the use of hydrogen bromide in acetic acid gives a high yield of the pure crystalline dibromide (IV), and the distillation of this intensely lachrymatory substance is thus avoided.

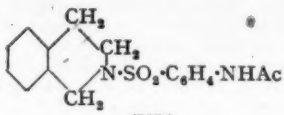
Our preparative method has now rendered the dibromide (IV) freely available and we have consequently investigated its synthetic application in several directions.

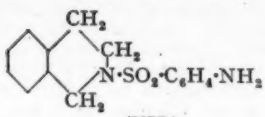
In view of the frequent occurrence of the reduced *iso*quinoline system in alkaloids possessing marked physiological activity, it was of interest to examine first the therapeutic effect of introducing this group into the sulphanilamide molecule.

For a preliminary testing of the method to be employed, an intimate mixture of equimolecular quantities of the dibromide (IV) and of *p*-toluenesulphonamide, together with excess of potassium carbonate, was heated at 160—170° for 30 minutes : the reaction proceeded smoothly, and the product readily yielded 2-p-*toluenesulphonyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (V). The same product was also obtained when the above mixture was boiled in alcoholic solution for 5 hours. Since this compound lacks the characteristic

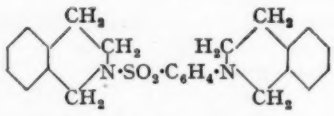
p-amino-group of the sulphanilamide molecule, it was not, of course, expected to possess marked anti-bacterial action.

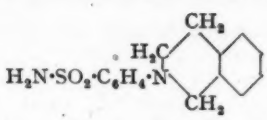

(V.)


(VI.)


(VII.)

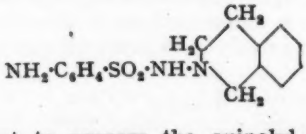
When, however, a similar mixture of the dibromide (IV), *p*-acetamidobenzenesulphonamide and potassium carbonate was boiled in alcohol, 2-p-*acetamidobenzenesulphonyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (VI) was obtained, and this compound was readily hydrolysed by hot dilute hydrochloric acid to the corresponding 2-p-*amino*-compound (VII). The latter could also be prepared by the condensation of equimolecular quantities of the dibromide (IV) and of sulphanilamide, but this method entailed the separation of the required *p*-amino-compound (VII) from the 2-[p-(2′-1′ : 2′ : 3′ : 4′-*tetrahydroisoquinolyl*)*benzenesulphonyl*]-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (VIII) which was always formed as a by-product: the method involving the hydrolysis of the acetamido-compound is therefore preferable. The di*iso*quinolyl compound (VIII) itself could of course be more readily prepared by the direct condensation of two molecules of the dibromide (IV) with one of sulphanilamide.

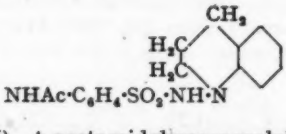
(VIII.) 


(IX.)

The preparation of p-(2-1 : 2 : 3 : 4-*tetrahydroisoquinolyl*)*benzenesulphonamide* (IX), isomeric with (VII), gave much greater difficulty than that of the previous derivatives. The condensation of the dibromide (IV) and sodium sulphanilate, followed by acidification, readily gave p-(2-1 : 2 : 3 : 4-*tetrahydroisoquinolyl*)*benzenesulphonic acid*, but the conversion of this acid into its *amide* (IX), although attempted under various conditions, was never satisfactory: the action of phosphorus pentachloride, followed by aqueous ammonia, furnished the pure amide, but only if small quantities were used, and even then in low yield. Consequently sufficient of this amide (IX) for adequate therapeutic tests was not obtained: this compound would probably be without anti-bacterial action, however, as almost all *p*-(disubstituted-amino)benzenesulphonamides are inert in this respect.

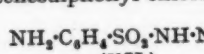
Two syntheses of *p*-aminobenzenesulphon-2-(1 : 2 : 3 : 4-tetrahydro*iso*quinolyl)amide (X) have been unsuccessfully attempted. An equimolecular mixture of the dibromo-compound (IV) and of *p*-acetamidobenzenesulphonhydrazide (Curtius and Stoll, *J. pr. Chem.*, **1926**, **112**, 125) underwent condensation in the presence of potassium carbonate, but the ultimate product was a glass from which no crystalline product could be obtained. Alternatively, many attempts were made to reduce 2-nitroso-1 : 2 : 3 : 4-tetrahydro*iso*quinoline to the 2-amino-compound, in order to condense the latter with *p*-acetamidobenzenesulphonyl chloride, but all such attempts failed in spite of a variety of conditions employed.

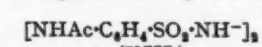
(X.) 

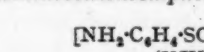

(XI.)

In an attempt to prepare the quinolyl isomeride of (X), *p*-acetamidobenzenesulphonyl chloride was condensed with 1-amino-1 : 2 : 3 : 4-tetrahydroquinoline to give p-*acetamidobenzenesulphon*-1-(1 : 2 : 3 : 4-*tetrahydroquinolyl*)*amide* (XI), but all attempts to hydrolyse the acetyl group from this compound caused extensive decomposition.

Since the therapeutic properties of the sulphaniiic hydrazides had not been recorded, the preparation of *p*-aminobenzenesulphonhydrazide (XII) by the hydrolysis of the *p*-acetamido-compound (Curtius and Stoll, *loc. cit.*) was first considerably improved. The *p*-acetamido-compound was then condensed with *p*-acetamidobenzenesulphonyl chloride in the presence of pyridine to give s.-*di*-p-*acetamidobenzenesulphonhydrazide* (XIII).


(XII.)


(XIII.)


(XIV.)

The constitution of this compound was shown by the fact that it was readily soluble in alkalis and insoluble in acids: the *as.*-isomeride, had it been formed, would have had these solubilities reversed. Hydrolysis then gave the s.-*di*-p-*amino*-compound (XIV) as a stable monohydrate.

Tests kindly carried out by Dr. G. Brownlee at the Wellcome Physiological Research Laboratories show that compounds (V), (VI), (VII), and (VIII) are almost without action on Staphylococcus and Streptococcus in a meat extract broth at 37°. The compounds (XI), (XII), and (XIV) were similarly tested with Staphylococcus, Streptococcus, *B. coli* and *B. typhosus*, and showed some bacteriostatic activity against the first: all three compounds, however, were completely inactive against Staphylococcus infection in mice.

Experimental.

Pure *o*-bromotoluene, prepared as described in *Organic Syntheses*, 1929, **9**, 22, an aqueous solution of sodium nitrite being used instead of the anhydrous salt, was obtained in 33% yield. In the bromination to *o*-bromobenzyl bromide, 85% of the theoretical quantity of bromine was used instead of 75% as recommended by Kenner and Wilson (*loc. cit.*): allowing for recovered unchanged material, the yield of pure *o*-bromobenzyl bromide (I) was 80% of the theoretical. This yield was obtained only if the bromine was added steadily during 3 hours without agitation of the reaction mixture.

o-Bromobenzyl Ethyl Ether (II).—*o*-Bromobenzyl bromide (190 g.) was added to a solution of sodium ethoxide prepared from sodium (20 g., 1·15 atoms) and absolute alcohol (450 c.c.) and chilled in ice-water. The mixture was refluxed until it had boiled for 15 minutes and developed an orange colour. Precipitated sodium bromide was removed from the hot solution, the latter concentrated, and the residual oil poured into water and repeatedly extracted with ether. Fractional distillation of the dried extract gave *o-bromobenzyl ethyl ether* as a colourless liquid, b. p. 119—120°/18 mm. (Found: C, 50·0; H, 5·0. $C_9H_{11}OBr$ requires C, 50·2; H, 5·1%): yield, 160 g., 98% of the theoretical.

o-β-Hydroxyethylbenzyl Ethyl Ether (III).—A mixture of fine magnesium filings (10 g.) and powdered iodine (5 g.) was triturated and then heated with continuous agitation in a long-necked flask until no more iodine vapour was evolved. The hot product was quickly and carefully (owing to its pyrophoric nature) transferred to a clean dry flask, which was corked until the product was cold. This activated magnesium was prepared immediately before use.

A solution of *o*-bromobenzyl ethyl ether (100 g.; 0·46 mol.) and ethyl bromide (17·4 g.; 0·16 mol.) in ether (200 c.c.) was added to the magnesium (24 g.; 1 atom) under ether (50 c.c.) at such a rate that the reaction, which started rapidly, kept the solvent gently boiling under reflux. When the addition was complete, boiling by external heating was maintained for 4 hours. The Grignard reagent was then chilled in ice–salt and continuously stirred while a solution of ethylene oxide (60 g.; 1·36 mols.) in ether (400 c.c.) was added in small portions (10 c.c.) during 4 hours. The product was set aside overnight and then again chilled and stirred while dilute sulphuric acid (600 c.c., 1 vol. of acid : 9 vols. of water) was slowly added. The product was filtered, and the ethereal solution washed in turn with water and sodium carbonate solution, dried (potassium carbonate), and fractionally distilled. The ether (III) was obtained having b. p. 152—155°/13 mm. (Found: C, 72·5; H, 8·7. Calc. for $C_{11}H_{16}O_2$: C, 73·3; H, 8·9%): yield, 29 g., 35% of the theoretical. Von Braun and Zobel (*loc. cit.*) give b. p. 149—152°/12 mm. This product, which could not be further purified by distillation, was used without further treatment for the preparation of the bromide (IV).

The fractional distillation of the above crude ether (III) always gave a lower fraction, b. p. 58°/14 mm., which on refractionation at atmospheric pressure gave a main fraction, b. p. 146—147°. Although analysis showed that the latter fraction was still a mixture, its chief component was ethylene bromohydrin, since with phenyl *iso*cyanate it readily gave phenyl-β-bromourethane, m. p. 74—75°, unchanged by admixture with a sample, m. p. 74—75°, prepared from pure ethylene bromohydrin (Found: C, 44·1; H, 4·2; N, 5·8. Calc. for $C_9H_{10}O_2NBr$: C, 44·3; H, 4·1; N, 5·7%).

o-β-Bromoethylbenzyl Bromide (IV).—A mixture of the hydroxy-ether (III) (22 g.) and a solution of hydrogen bromide in acetic acid (90 g., containing 50 g. of HBr/100 c.c. of solution) in a stoppered bottle was immersed in a boiling water-bath for 24 hours. The cold product was poured into water (*ca.* 1 l.), the heavy dark oil, which usually solidified, extracted with ether, and the extract washed in turn with aqueous sodium carbonate and water, and dried. Distillation of the ether left the oily dibromide, which readily solidified: yield, 34 g., 90%. Recrystallisation from light petroleum (b. p. 40—60°) (charcoal) gave the dibromide in colourless needles, m. p. 51—53°, and this product was used without further treatment for subsequent synthetic work. Further recrystallisation from alcohol gave the pure material, m. p. 53° (Found: C, 38·55; H, 3·8. Calc. for $C_9H_{10}Br_2$: C, 38·9; H, 3·6%): von Braun and Zobel also give m. p. 53°.

2-p-*Toluenesulphonyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (V).—An intimate powdered mixture of the dibromide (IV) (2·8 g.), *p*-toluenesulphonamide (1·7 g.; 1 mol.), and anhydrous potassium carbonate (2·1 g.; 1·5 mols.) was heated in an oil-bath to 160° and the temperature then kept at 160—170° for 30 minutes: the reaction started at about 90° with carbon dioxide evolution. The cold hard mass was pulverised and extracted with boiling alcohol, which after filtration and cooling deposited the p-*toluenesulphonyl* derivative (V) in colourless needles (2·5 g.), m. p. 141—142°, increased to 142° by one recrystallisation from alcohol (Found: C, 66·8; H, 6·05; N, 4·8. $C_{16}H_{17}O_2NS$ requires C, 66·9; H, 5·9; N, 4·9%).

2-p-*Acetamidobenzenesulphonyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (VI).—A mixture of the dibromide (IV) (2·8 g.), *p*-acetamidobenzenesulphonamide (2·1 g.; 1 mol.), anhydrous potassium carbonate (4·1 g.; 3 mols.), and alcohol (20 c.c.) was refluxed for 5 hours. The liquid was filtered hot, and the residue extracted with boiling alcohol (20 c.c.). The combined alcoholic solutions deposited the colourless crystalline p-*acetamido*-derivative (VI), m. p. 170—174° (3·3 g.): two recrystallisations from alcohol, followed by heating in a vacuum at 100°, gave the pure compound, m. p. 175—176° (Found: C, 61·6; H, 5·9; N, 8·2. $C_{17}H_{18}O_3N_2S$ requires C, 61·8; H, 5·45; N, 8·5%).

2-p-*Aminobenzenesulphonyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (VII).—(A) *By hydrolysis of the acetyl derivative.* A mixture of the above acetyl derivative (VI) (6 g.) and dilute hydrochloric acid (90 c.c., 1 vol. of conc. acid : 3 vols. of water) was refluxed for 1·5 hours. After cooling, the crude solid was collected, boiled with 8% sodium carbonate solution (120 c.c.), again collected, washed with water, dried, and recrystallised from benzene containing a small quantity of alcohol. The p-*aminobenzene* derivative (VII) was thus obtained as colourless crystals, which, after heating in a vacuum at 100° to eliminate traces of solvent, had m. p. 174° with softening at 172° (Found: C, 62·4; H, 5·5; N, 9·7. $C_{15}H_{16}O_2N_2S$ requires C, 62·5; H, 5·55; N, 9·7%): a mixture with unchanged acetyl compound had m. p. 164—170°.

(B) *By direct condensation.* A mixture of the dibromide (IV) (2·8 g.), sulphanilamide (1·7 g.; 1 mol.), potassium carbonate (4·1 g.; 3 mols.), and alcohol (20 c.c.) was refluxed for 5 hours and filtered, and the residue further extracted with hot alcohol. The united alcoholic solutions on cooling deposited crystals, which were purified precisely as in (A) above, except that three recrystallisations were now necessary. The final product had m. p. identical with that in (A), both mixed and unmixed.

The insoluble residue from the above alcoholic extraction, when washed with water to remove inorganic material, furnished the di*iso*quinolyl compound (VIII) described below, being identified (after purification) by analysis (Found: N, 7·1%) and mixed m. p. determination.

2-[p-(2′-1′ : 2′ : 3′ : 4′-*Tetrahydroisoquinolyl*)*benzenesulphonyl*]-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (VIII).—The condensation described in (B) above was repeated, only half the sulphanilamide (0·5 mol.) being used. The solid residue insoluble in boiling alcohol was washed thoroughly with water and recrystallised from alcoholic acetone, the *compound* (VIII) being obtained in colourless crystals, m. p. 153—156° (Found: C, 71·4; H, 6·0; N, 7·0. $C_{24}H_{24}O_2N_2S$ requires C, 71·3; H, 5·9; N, 6·9%). The m. p. of this compound showed inexplicable variations. For instance, the above pure sample, after being kept in a vacuum desiccator for 1 week, softened at 140° and had m. p. 142—144°: another pure sample, similarly kept for 3 weeks, melted at 141—142° to an opaque liquid which became clear at 153—154°, although the composition was unaltered (Found: N, 6·9%). The pure material, after recrystallisation from benzene–*cyclo*hexane, softened at 144° and melted at 149°; after recrystallisation from carbon tetrachloride, it softened at 153° and melted at 157—157·5°. All m. p.'s were determined under approximately identical conditions.

p-(2-1 : 2 : 3 : 4-*Tetrahydroisoquinolyl*)*benzenesulphonamide* (IX).—A mixture of the dibromide (IV) (2·8 g.), sodium sulphanilate (1·9 g.; 1 mol.), anhydrous sodium carbonate (4·3 g.; 4 mols.), and alcohol (20 c.c.) was boiled for 6 hours and cooled. The solid residue was twice recrystallised from hot water: the colourless crystals of the sodium sulphonate corresponding to (IX) thus obtained were redissolved in hot water; the solution, when acidified with hydrochloric acid, deposited the crystalline p-(2-1 : 2 : 3 : 4-*tetrahydroisoquinolyl*)*benzenesulphonic acid*, which was washed with a small quantity of boiling water and twice recrystallised from much boiling water, in which it was only slightly soluble: it was thus obtained as a microcrystalline *hemihydrate*, m. p. 236—237° (efferv.) (Found: C, 60·3; H, 5·5; N, 4·6. $C_{15}H_{15}O_3NS,\frac{1}{2}H_2O$ requires C, 60·4; H, 5·4; N, 4·7%).

An intimate powdered mixture of the above acid (1·1 g.) and phosphorus pentachloride (0·8 g.; 1·04 mol.) was heated at 120° for 15 minutes, hydrogen chloride being evolved. The cold brown hard product was powdered, added to aqueous ammonia (*d* 0·880, 30 c.c.), and the mixture heated on a boiling water-bath for 30 minutes. The brown powder so obtained was collected, washed with water, and dried: it was freely soluble in cold dilute sodium hydroxide solution or hydrochloric acid, and was reprecipitated from each solution on neutralisation. This powder was dissolved in hot ethyl alcohol, a small quantity of brown microcrystalline material which separated on cooling was removed, and the filtrate taken to dryness. The residue, twice recrystallised from methyl alcohol (charcoal), gave the *sulphonamide* (IX) in pale brown needles, which softened at 161°, melted at 163°, resolidified and remelted at 182—184°: even after heating in a vacuum at 100° for 3 hours, this behaviour was unchanged, and it was therefore not due to solvent of crystallisation (Found for the unheated material: C, 62·6; H, 5·8; N, 9·6. $C_{15}H_{16}O_2N_2S$ requires C, 62·5; H, 5·55; N, 9·7%).

Attempted Preparation of the Amide (X).—(i) A mixture of *p*-acetamidobenzenesulphonhydrazide (2·3 g.), the dibromide (IV) (2·8 g.; 1 mol.), potassium carbonate (4 g.; 2·9 mols.), and absolute alcohol (50 c.c.) was refluxed for 8 hours, and then filtered hot from the entirely inorganic residue. The filtrate was evaporated on a water-bath, giving a very viscous oil which set to a glass on cooling. The glass contained nitrogen and sulphur, but no halogen: it did not crystallise even after several months, and no crystalline constituent or derivative could be isolated.

(ii) 2-Nitroso-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, m. p. 51—53°, was prepared by Bamberger and Dieckmann's method (*Ber.*, 1893, **26**, 1211). The reduction of this compound was attempted (*a*) in alcoholic acetic acid with zinc dust, (*b*) in neutral alcoholic solution with aluminium amalgam (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **107**, 86): although the temperature and concentrations were varied over wide limits, complete reduction to 1 : 2 : 3 : 4-tetrahydro-*iso*quinoline always occurred.

p-*Acetamidobenzenesulphon*-1-(1 : 2 : 3 : 4-*tetrahydroquinolyl*)*amide* (XI).—(*a*) 1 : 2 : 3 : 4-Tetrahydroquinoline was prepared by Oldham and Johns's method (*J. Amer. Chem. Soc.*, 1939, **61**, 3289), b. p. 121°/13 mm.; hydrochloride, m. p. 180—182°. (*b*) No specific directions for the next two stages have been published. A solution of sodium nitrite (10·7 g.) in water (50 c.c.) was slowly added with stirring and external cooling to a solution of tetrahydroquinoline (20 g.; 1 mol.) in concentrated hydrochloric acid (38 c.c.) diluted with water (60 c.c.) and ice (50 g.), the temperature being kept below 10° throughout. One hour after the addition, the yellow oily 1-nitroso-1 : 2 : 3 : 4-tetrahydroquinoline (22 g., 92%) was extracted with ether, dried (potassium carbonate), and, after removal of the ether, reduced without further purification (cf. Ziegler, *Ber.*, 1888, **21**, 862). (*c*) The nitroso-compound (22 g.), dissolved in a mixture of acetic acid (45 c.c.), water (45 c.c.), and alcohol (70 c.c.), was slowly added to a vigorously stirred suspension of zinc dust (100 g.) in 90% alcohol (130 c.c.) maintained at 60—75°. When reduction was complete, the filtered solution was evaporated under reduced pressure to remove alcohol, treated with 30% caustic soda solution until the zinc hydroxide redissolved, and then extracted with ether. The ethereal solution was shaken with dilute sulphuric acid (50 c.c., 1 vol. of acid : 9 vols. of water), and the precipitated 1-amino-1 : 2 : 3 : 4-tetrahydroquinoline sulphate collected and recrystallised from water: yield, 11 g. Treatment with alkali gave the 1-amino-base, m. p. 53—55° (cf. Hofmann and Koenigs, *Ber.*, 1883, **16**, 730; Barger and Dyer, *J. Amer. Chem. Soc.*, 1938, **60**, 2414). (*d*) The aminotetrahydroquinoline sulphate (4·3 g.) was added to a vigorously stirred solution of caustic soda (2·8 g.; 7 mols.) in water (80 c.c) maintained at 60°, and *p*-acetamidobenzenesulphonyl chloride (5·1 g.; 2·6 mols.) then slowly added, the stirring being continued for 1 hour. The solid which had separated was collected, and purified by dissolution in warm aqueous 10% caustic soda, filtration, and reprecipitation with hydrochloric acid: a second crop was obtained by acidifying the original mother-liquor. The united crops were extracted with sodium carbonate solution, and the crude insoluble product (3 g.), after recrystallisation from much alcohol, gave p-*acetamidobenzenesulphon*-1-(1 : 2 : 3 : 4-*tetrahydroquinolyl*)*amide* in colourless crystals, m. p. 203° (decomp.) (Found: C, 59·1; H, 5·8; N, 12·3. $C_{17}H_{19}O_3N_3S$ requires C, 59·1; H, 5·6; N, 12·2%).

The attempted hydrolysis of this compound, hydrochloric acid or caustic soda being used with a wide variety of concentration and time of heating, always gave either unchanged material or extensive decomposition, and the required *p*-amino-compound could not be isolated.

p-*Aminobenzenesulphonhydrazide* (XII).—The following preparative method was employed, as Curtius and Stoll's directions (*loc. cit.*) always gave unchanged material. A smooth paste of powdered *p*-acetamidobenzenesulphonhydrazide (5 g.) and concentrated hydrochloric acid (8 c.c.) was stirred mechanically while heated on a boiling water-bath. Five minutes' heating gave a clear solution, which after a further 7 minutes was cooled, neutralised with 3% caustic soda solution, and kept at 0° for 1 hour. The precipitated material was twice recrystallised from 50% aqueous alcohol, and the *p*-amino-compound (XII) obtained as colourless crystals (1·2 g., 29%), m. p. 132° (efferv.) (Found: C, 38·5; H, 4·8; N, 22·7. Calc. for $C_8H_9O_2N_3S$: C, 38·5; H, 4·8; N, 22·4%).

s.-*Di*-p-*acetamidobenzenesulphonhydrazide* (XIII).—*p*-Acetamidobenzenesulphonyl chloride (4·6 g.) was added to a solution of the *p*-acetamido-hydrazide (4·6 g.; 1 mol.) in dry pyridine (20 c.c.), and the solution heated at 100° for 30 minutes, cooled, and poured into water (400 c.c.). The white microcrystalline precipitate was collected, washed with water, and, since it was insoluble in all the usual organic liquids, purified by dissolution in N-sodium hydroxide (50 c.c.), filtration, and reprecipitation with dilute hydrochloric acid. The *di*-p-*acetamido*-compound (XIII) (3·75 g., 44%) so obtained, when washed with boiling water and alcohol and dried, was unaffected by heating to 300° (Found: C, 45·1; H, 4·5; N, 13·1. $C_{16}H_{18}O_6N_4S_2$ requires C, 45·1; H, 4·2; N, 13·1%).

s.-*Di*-p-*aminobenzenesulphonhydrazide* (XIV).—A mixture of the acetamido-compound (XIII) (4 g.), concentrated hydrochloric acid (15 c.c.), and water (30 c.c.) was refluxed for 4 hours. After a further short boiling with charcoal, filtration gave a colourless solution. This was treated with a solution of caustic soda (5 g.) in water (15 c.c.) and then with saturated aqueous sodium carbonate until alkaline. The precipitated *di*-p-*amino*-compound (XIV) (2·3 g., 72%) was collected, washed with water, and recrystallised from 50% aqueous alcohol, from which it separated as a stable crystalline *monohydrate*: the latter lost water slowly in a vacuum over sulphuric acid, and readily when heated at 135—140°/15 mm., but the anhydrous material rapidly re-formed the hydrate on exposure to air (Found for the monohydrate: C, 39·8; H, 4·6; N, 15·4; S, 18·1; H_2O, 5·15. $C_{12}H_{14}O_4N_6S_2,H_2O$ requires C, 40·0; H, 4·4; N, 15·55; S, 17·8; H_2O, 5·0%. Found for the anhydrous substance: N, 16·1. $C_{12}H_{14}O_4N_6S_2$ requires N, 16·4%). Both the anhydrous material and the hydrate darkened at 190° and melted at 203° (decomp.).

Dr. Brownlee reports: The compounds (XI), (XII), and (XIV) were tested *in vitro* at various concentrations against

constant inocula of Streptococcus, Staphylococcus, *B. coli* and *B. typhosus* (1000—2000 per c.c.). Owing to their low solubility, the highest concentrations obtainable were 1/12,500 for (XI) and 1/2500 for (XII) and (XIV). All three compounds showed bacteriostatic activity against Staphylococcus, arresting growth for 18 hours—after this period the culture developed when (XI) was at its highest concentration (1/12,500) and when (XII) and (XIV) were at a concentration of 1/5000, but showed no visible growth even after 48 hours when (XII) and (XIV) were at their highest concentration (1/2500).

When tested against Staphylococcus infection in mice, using doses of 10 mg. of (XI) and (XIV) per 20 g. of mouse, and of 5 mg. of (XII) per 20 g., all three compounds were completely inactive.

The compounds were tested for toxicity, and compound (XII), as was to be expected of a hydrazide, was lethal at a dose of 100 mg. per 20 g. of mouse, but (XI) and (XIV) were not.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, September 19th*, 1942.]

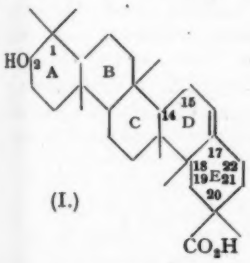
---

161. *Sapogenins. Part XVII. The Position of the Carboxyl Group in Oleanolic and Glycyrrhetic Acids.*

By GEORGE A. R. KON and WALTER C. J. ROSS.

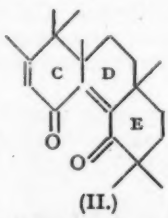
Methyl acetyloleanolate and methyl acetyldeoxoglycyrrhetate on treatment with selenium dioxide give isomeric acetyl dehydrodiketo-esters, both of which undergo alkaline hydrolysis with the loss of the carbomethoxy-group. Both are therefore β-ketonic esters; this shows that the carboxyl group in the parent acids must occupy the same position in the molecule and cannot be attached to a ring junction, as already deduced from measurements of surface films (Bilham, Kon, and Ross, this vol., p. 535). The experiments thus afford an independent chemical confirmation of the earlier results and incidentally also of the formulæ recently put forward (*loc. cit.*, p. 532).

THE appearance of a paper by Ruzicka and Jeger (*Helv. Chim. Acta*, 1942, **25**, 775) makes it desirable to place on record certain experiments, which, though still incomplete, afford a purely chemical confirmation of the formulæ recently put forward for deoxoglycyrrhetic and oleanolic acids, both of which are represented by formula (I) and differ by the configuration of the groups attached to C_{20} (Bilham, Kon, and Ross, this vol., p. 535).

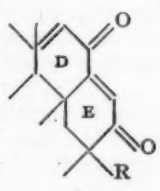


(I.)

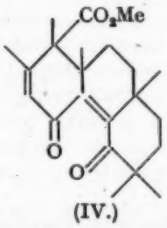
The compound known as Jacobs's keto-diol has recently been shown to be a hydroxy-dione (Ruzicka and Jeger, *Helv. Chim. Acta*, 1941, **24**, 1257) and the formation of its esters from β-amyrin esters takes place in three ways: (i) by the permanganate oxidation of the thio-compounds formed from β-amyrin or its benzoate and sulphur (Jacobs and Fleck, *J. Biol. Chem.*, 1930, **88**, 137; Simpson, J., 1938, 1313), (ii) by the action of selenium dioxide on amyradienol I (Picard and Spring, J., 1941, 35), and (iii) as a by-product in the action of selenium dioxide on β-amyrin acetate, amyradienol II being formed at the same time (Ruzicka and Jeger, *loc. cit.*); the same compound is also formed by the futher action of selenium dioxide on amyradienol II (Ruzicka, Jeger, and Norymberski, *ibid.*, 1942, **25**, 457).* Ruzicka and Jeger conclude from the reaction of the compound with hydrazine that it is a 1 : 4-diketone and formulate it as (II) on the basis of the Haworth triterpene formula; on the assumption of the new formula (I) it will be represented by the partial structure (III, R = Me).



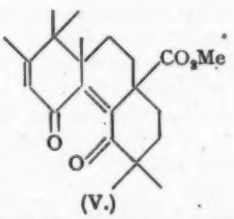
(II.)



(III.)



(IV.)



(V.)

Compounds analogous to Jacobs's hydroxy-dione can also be derived from methyl oleanolate and from methyl deoxoglycyrrhetate; both will be represented by the same formula (III, R = CO_2Me) if (I) correctly represents the parent acids, and will be β-ketonic esters. The older formulations would, on the other hand, lead to the structures (IV) and (V) respectively.

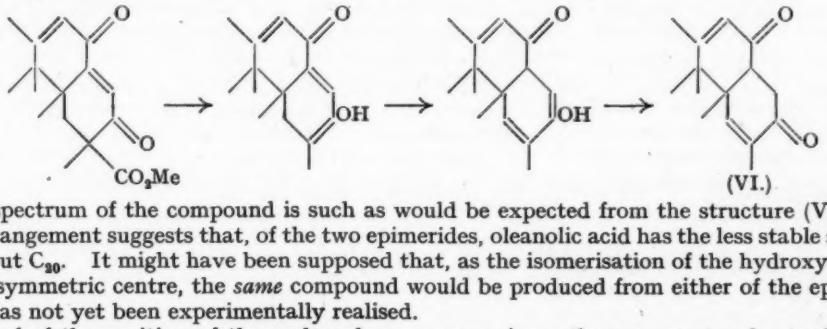
An ester with properties similar to those of Jacobs's hydroxy-dione acetate is formed in good yield on treatment of methyl acetyldeoxoglycyrrhetate with selenium dioxide in acetic acid solution; it becomes the sole product of the reaction if the amount of selenium dioxide is increased, otherwise it is accompanied by methyl acetyldehydrodeoxoglycyrrhetate (compare Bilham, Kon, and Ross, *loc. cit.*); it is also produced from the latter compound by the action of selenium dioxide. The diketo-ester is readily hydrolysed by alkali to the *acid* $C_{30}H_{42}O_5$, which is accompanied by a neutral *diketone* $C_{29}H_{42}O_3$, formed by the spontaneous decarboxylation of the acid; the same diketone is also produced by the decarboxylation of the acid on heating. These results clearly indicate that the parent compound must be a β-ketonic ester; an account of them was ready for

* The authors are greatly indebted to Professor Ruzicka for reprints of this and the preceding paper, which have only recently become available in this country.

publication when it was anticipated by the appearance of Ruzicka and Jeger's last paper, in which the diketo-ester and its hydrolysis products are described, the experimental data being in excellent agreement with ours.

Now an *ester* exactly similar to the above is also formed from methyl acetyloleanolate. A compound of the expected composition has already been briefly mentioned by Ruzicka, Grob, and Sluys-Veer (*Helv. Chim. Acta*, 1939, **22**, 788), who obtained it as a by-product in the preparation of the dehydro-ester, but did not investigate it. It has also been prepared by us in this way and by the action of selenium dioxide on the dehydro-ester; the pure compound melts somewhat higher than found by the Swiss authors, namely, at 247—248° (uncorr.), and is lævorotatory, $[\alpha]_D$ −144°. Their figure for $[\alpha]_D$, 146°, must, we think, be due to a misprint, as is that for the dehydro-ester, which also is lævorotatory. The absorption spectrum of this ester is entirely similar to that of its isomeride (maxima at 2790 A. and 2250 A., log $\varepsilon_{max.}$ 4·11 and 3·84); on alkaline hydrolysis it yields an acid $C_{30}H_{42}O_5$ and a neutral compound $C_{29}H_{42}O_3$. These two compounds are identical with the hydrolysis products obtained by Jacobs and Fleck (*J. Biol. Chem.*, 1932, **96**, 341) from the benzoate of an ester obtained essentially by route (i) above. The presence of a 1 : 4-diketone grouping in these compounds follows from the conversion of the C_{30}-acid into a *pyridazine* derivative on heating with hydrazine hydrate. This compound is evidently formed with the elimination of the carboxyl group and has the formula $C_{29}H_{42}ON_2$; this, and the production of the neutral diketone on hydrolysis of the ester, shows that the latter must be a β-ketonic ester, a conclusion already tentatively expressed by Jacobs and Fleck. It follows that the carboxyl group of oleanolic and of glycyrrhetic acid must occupy the same position in the molecule, in agreement with formula (III), but not (IV) or (V).

There is an interesting difference between the hydroxy-diones derived from the two epimeric esters: the compound obtained from acetyldeoxoglycyrrhetic ester is in every way similar to the diketo-ester from which it is derived, has a similar absorption spectrum and can be described as the lower homologue of Jacobs's hydroxy-dione. The isomeride derived from acetyloleanolic ester is much less soluble and, unlike the lævorotatory parent compound, it is strongly dextrorotatory. Also, its absorption spectrum is quite different: the maximum lies at 2390 A., not *ca.* 2790 A., as in all the other compounds of this type, and the intensity is appreciably higher (log $\varepsilon_{max.}$ = 4·27). A secondary maximum at 3100 A. (log $\varepsilon_{max.}$ = 2·30) shows that the selective absorption is attributable to an αβ-unsaturated ketone grouping or groupings (compare, *e.g.*, the absorption of cholestenone; Jones, Wilkinson, and Kerlogue, this vol., p. 391). It is clear that the chromophore originally present in both the β-ketonic esters and in Jacobs's hydroxy-dione must have undergone a rearrangement. This only takes place after removal of the blocking carbomethoxy-group and it is reasonable to suppose that it involves the carbon atom bearing this group; it may be pictured as a process of enolisation, followed by rearrangement, thus:

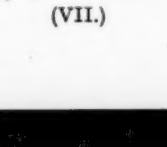


(VI.)

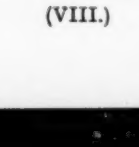
The absorption spectrum of the compound is such as would be expected from the structure (VI); the occurrence of the rearrangement suggests that, of the two epimerides, oleanolic acid has the less stable stereochemical arrangement about C_{20}. It might have been supposed that, as the isomerisation of the hydroxy-dione appears to involve this asymmetric centre, the *same* compound would be produced from either of the epimeric diketo-esters, but this has not yet been experimentally realised.

With the proof of the position of the carboxyl group now given, the arguments advanced in Part XIII (this vol., p. 532) in support of the new position of the double bond in β-amyrin and the related acids gain additional weight, since they are to a great extent contingent on the position of the carboxyl group in the latter compounds.

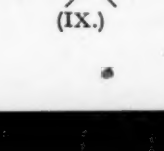
In Part XIV (this vol., p. 535) it was suggested that the carbonyl group of glycyrrhetic acid occupies a position on C_{22} because the acid is reduced by sodium and alcohol to the lævorotatory dehydro-acid (VII ⟶ VIII, R = CO_2H), exactly like keto-oleanolic acid, in which the position of the carbonyl group is established by the surface-film method and also by its relationship with siaresinolic acid. It was hoped to obtain additional evidence on this point from the most recent experiments of Ruzicka and Jeger (*loc. cit.*), who succeeded in introducing an additional double bond into methyl acetylglycyrrhetate by the method previously used with keto-β-amyrin (Picard and Spring, *loc. cit.*).



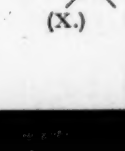
(VII.)



(VIII.)



(IX.)



(X.)

Our own attempts to achieve this had failed because a bromine-containing compound was obtained (Bilham, Kon, and Ross, *loc. cit.*); this is exclusively formed under mild conditions and is now found to be a saturated *dibromide*, resulting from the addition of bromine to the double bond. This reaction, which may be of some interest from the point of view of triterpene chemistry, is analogous to the formation of the dibromide from 6-keto-3-acetoxy-Δ^4-cholestene (Jackson and Jones, J., 1938, 1406); the compound itself is remarkable owing to its unusually high rotation ($[\alpha]_D$ +521°). Under vigorous conditions the dehydro-ester described by Ruzicka and Jeger is also obtained, and it also results from the debromination of the dibromide with pyridine.

The introduction of an additional double bond into the structure (VII) will give rise to a compound (IX) with two double bonds in one ring, as in amyradienol I. This, and other similar compounds, is characterised by a high positive rotation. The new dehydro-compound has $[\alpha]_D$ +321° (as against 282°, the figure given by Ruzicka and Jeger) and amyradienonyl acetate has $[\alpha]_D$ +336° (Ruzicka, Jeger, and Norymberski, *loc. cit.*), in agreement with this formulation. However, the absorption spectra of these compounds are in better agreement with the alternative formula (X), as is the formation of amyradienonol from amyradienol II on oxidation with lead tetra-acetate; the formation of amyrenonyl acetate from amyradienyl II acetate (Picard and Spring, *loc. cit.*) also becomes intelligible if the carbonyl group is placed on C_{16}.

A simple way of settling these discrepancies would be the elimination of the carbonyl group in the dehydro-ester, which should give rise to the known acetyldehydrodeoxoglycyrrhetic ester (VIII, R = CO_2Me) if it has the structure (X), or to a new ester analogous to amyradienol I. Reduction of the ester with hydrazine and sodium ethoxide gave uncrystallisable products. Catalytic reduction gave a crystalline product, but this proved to be a mixture; it had no selective absorption of light, showing that the unsaturated system had undergone reduction. Finally, reduction by the Clemmensen method proceeded easily, but the elimination of the carbonyl group was accompanied by the reduction of one of the double bonds, a phenomenon recently observed in other cases (Parts XV and XVI, this vol., pp. 540, 544). These experiments are therefore inconclusive and further work is in progress.

Experimental.

Unless otherwise stated, analysis specimens were dried for 2 hours at 100°/1—2 mm.; m. p.'s were determined in sealed capillaries and are uncorrected; rotations were determined in chloroform solution, and absorption spectra in alcoholic solution.

Diketo-dehydro-ester from Oleanolic Acid (III).—300 Mg. of methyl acetyldehydro-oleanolate (compare Bilham, Kon, and Ross, *loc. cit.*) were boiled overnight with 150 mg. of selenium dioxide and 20 c.c. of AnalaR acetic acid. The solution was diluted with *ca.* 4 vols. of benzene, extracted with alkali, washed, dried, and percolated through an 8 cm. column of activated alumina, the latter being washed with benzene until no more solid was recovered on evaporation; this gave some 40 mg. of unchanged dehydro-ester contaminated with selenium.

Elution of the column with ether gave the *diketo*-ester as a yellow oil which rapidly solidified and was practically free from selenium; it crystallised from methyl alcohol or from petroleum–benzene in plates (Found: C, 73·8; H, 8·8. $C_{32}H_{46}O_6$ requires C, 73·6; H, 8·6%); the properties of the compound are given on p. 742.

Several grams of residues from the preparation of the dehydro-ester were similarly purified and subjected to separation by the chromatographic method, a long column being used. After elution of the diketo-ester an even more strongly adsorbed fraction was obtained in small amount; this was repeatedly recrystallised from methyl alcohol, forming needles, m. p. 198—199°, consisting of methyl oleanolate, evidently formed by the hydrolysis of its acetate (Found: C, 78·9; H, 10·7. Calc.: C, 79·1; H, 10·7%). The diketo-ester was purified as before (Found: C, 73·5; H, 8·5%); it gave a very faint yellow colour with tetranitromethane.

Hydrolysis. 500 Mg. of the ester were boiled for 4 hours with 1·5 g. of potassium hydroxide in 1·5 c.c. of water and 20 c.c. of alcohol; a deep yellow colour gradually developed. The hot solution was gradually diluted, and the crystalline precipitate recrystallised from slightly diluted alcohol, forming fine needles (250 mg.), m. p. 286—289°, $[\alpha]_D$ +204° (c = 1·67 in pyridine; compare Jacobs and Fleck, *loc. cit.*); it was rather sparingly soluble in acetone, the solvent recommended by Jacobs and Fleck (Found: C, 79·2, 79·1; H, 10·2, 9·9. Calc.: C, 79·4; H, 9·7%).

The alkaline mother-liquors from which the above hydroxy-diketone had been removed were acidified; the hydroxy-acid then deposited decomposed very easily even on drying at 80°. A specimen crystallised from aqueous methyl alcohol had m. p. 262—264° (lit., 268—269°) and an absorption maximum at *ca.* 2800 A. (Found for a specimen dried at room temperature in a high vacuum: C, 74·0; H, 9·2. Calc.: C, 74·7; H, 8·8%); when melted, the acid was converted into the hydroxy-diketone, which was identified by its m. p., mixed m. p., and absorption spectrum.

Pyridazine derivative. 60 Mg. of the above acid were heated overnight in a sealed tube at 200° with 1 c.c. of 98% hydrazine hydrate and 5 c.c. of alcohol. The *pyridazine* derivative, recovered by extraction with ether and evaporation of the washed and dried extract, crystallised from ethyl acetate–light petroleum in felted needles, m. p. 263—265°; the crude compound rapidly assumed a reddish tinge on exposure to light (Found: C, 80·0; H, 10·2. $C_{29}H_{42}ON_2$ requires C, 80·1; H, 9·7%).

Oxidation of the hydroxy-ketone. 550 Mg. of the hydroxy-diketone in 20 c.c. of AnalaR acetic acid were treated with 300 mg. of chromic acid in 1 c.c. of water and 5 c.c. of acetic acid. After ½ hour the solution was warmed to 60° and gradually diluted, the crystalline precipitate being collected and washed with water. The *triketone* crystallised from dilute alcohol in small needles (220 mg.) melting rather indefinitely above 300° (decomp.) (Found: C, 79·3; H, 9·3. $C_{29}H_{40}O_3$ requires C, 79·8; H, 9·3%). The triketone was reduced by Clemmensen's method, but a homogeneous product could not be isolated.

Diketo-dehydro-ester from Deoxoglycyrrhetic Acid.—This preparation was carried out as described above and the product was purified in the same way. It was obtained free from the dehydro-ester and in 75% yield when 2 g. of acetyldeoxoglycyrrhetic ester were boiled overnight with 3 g. of freshly sublimed selenium dioxide in 100 c.c. of AnalaR acetic acid. The *diketo*-ester crystallised from light petroleum (b. p. 60—80°), containing a little benzene, in plates, m. p. 236—237° (Found: C, 73·8; H, 9·2. $C_{32}H_{46}O_6$ requires C, 73·6; H, 8·6%).

Hydrolysis. This was carried out as described above, but owing to its greater solubility the neutral compound did not separate from the solution. This was therefore evaporated under reduced pressure, and the residue extracted with water; acidification of the aqueous solution gave the *acid*. The sandy insoluble material was recrystallised from dilute acetone (yield, 15%), forming plates, m. p. 248—249°, $[\alpha]_D$ −39° (c = 0·46). Light absorption: maxima at 2785 and 2250 A. (log $\epsilon_{max.}$ 4·11 and 3·74) (Found: C, 79·4; H, 9·7. $C_{29}H_{42}O_3$ requires C, 79·4; H, 9·8%). The same

hydroxy-diketone was also obtained when the acid mentioned above was melted, but the purification of the product proved very wasteful.

The acid obtained above (yield, 60%) could be crystallised from dilute acetone; it melted partially at 184—185° and completely at *ca.* 245°, the latter being the m. p. of the hydroxy-diketone (Found: C, 74·4; H, 9·1. $C_{30}H_{42}O_5$ requires C, 74·7; H, 8·8%).

Bromination of Methyl Acetylglycyrrhetate.—This was carried out as described in Part XIV (*loc. cit.*), a 5% solution of bromine being used. At *ca.* 85°, or essentially under the conditions used by Ruzicka and Jeger, the only product formed was the bromo-ester described, but not analysed, in our previous paper. The product was conveniently precipitated by gradual dilution of the hot solution, separating in a crystalline condition. After repeated crystallisation from methyl alcohol the *dibromo*-ester decomposed at 215—220°, $[\alpha]_D$ +521° (c = 0·925); it gave no colour with tetranitromethane and had no selective absorption of light (Found: C, 58·5; H, 7·2. $C_{32}H_{48}O_5Br_2$ requires C, 57·9; H, 7·1%). When the bromination was conducted at the b. p. and as rapidly as possible, the product was usually a mixture, from which the less soluble dibromo-ester separated first, the dehydro-ester being obtained from the later crops. On one occasion it was the only product formed. It was also obtained by boiling the dibromo-ester with 20 parts of dry pyridine for ½ hour and precipitation with dilute acid; the coloured product was recrystallised from dilute methyl alcohol (charcoal) and formed small needles, m. p. 241—242°, $[\alpha]_D$ +321° (c = 1·425); the absorption spectrum showed a maximum at 2795 A., log $\epsilon_{max.}$ 4·10 (Found: C, 75·2; H, 9·5. Calc.: C, 75·5; H, 9·2%).

Reduction of the Dehydro-ester.—(i) 500 Mg. of the ester in 16 c.c. of hot acetic acid were added to 6 g. of amalgamated zinc. On the addition of 4 c.c. of hydrochloric acid a vigorous reaction occurred; after a few minutes' boiling most of the *ester* had separated from the solution. After ½ hour it was isolated by dilution and dissolved in benzene, the solution washed with alkali, dried, and percolated through a column of activated alumina, which was then well washed with benzene. The ester recovered by evaporation of the benzene solution was recrystallised from methyl alcohol, forming small plates, m. p. 258—259°; it gave a yellow colour with tetranitromethane and was optically transparent, $[\alpha]_D$ +127° (c = 1·13) (Found: C, 77·1; H, 10·4. $C_{32}H_{52}O_4$ requires C, 77·3; H, 10·2%).

(ii) The dehydro-ester was shaken with 100 parts of AnalaR acetic acid and ½ of it weight of Adams's catalyst, which had been previously reduced, for 18 hours. The ester, isolated in the usual way, was a crystalline solid, but it was evidently a mixture of reduction products; it was therefore dissolved in benzene, and the solution percolated through a column of activated alumina. Practically the whole of the product was found in the portion which had not been adsorbed, although a little material was recovered when the column was eluted with ether. The main portion was crystallised alternately from slightly diluted methyl alcohol and from petroleum; after numerous crystallisations nacreous plates still melting rather indefinitely at 222—224° with previous sintering were obtained, having practically no optical rotation and no selective absorption of light (Found: C, 75·9, 75·7; H, 10·0, 9·9%) and giving a yellow colour with tetranitromethane.

(iii) 500 Mg. of the dehydro-ester were heated overnight to 200° with 1·3 c.c. of 98% hydrazine hydrate and 10 c.c. of 5% sodium ethoxide solution. The acid recovered on acidification and extraction was a pale yellow gum; it was esterified with diazomethane, and the ester acetylated by warming with 10 parts of acetic anhydride and 10 parts of dry pyridine for a short time. After several hours the acetylated product was recovered by dilution and purified by percolation of a benzene solution through activated alumina. The ester was recovered as a colourless gum which did not solidify and gave a brownish-yellow colour with tetranitromethane.

The authors are indebted to Mr. J. T. McCombie for measuring the absorption spectra.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7. [*Received, September 5th,* 1942.]

---

162. *The Preparation of Symmetrical Azo-compounds, the Positional Influence of the Nitro-group on the Decomposition of Nitronaphthalenediazonium Sulphates by Cuprous Hydroxide, and an Improved Method for the Production of 2-Nitronaphthalene.*

By HERBERT H. HODGSON, ERIC LEIGH, and GERALD TURNER.

The decomposition of diazonium salts in sulphuric acid solution with cuprous hydroxide depends on the positivity of the carbon atom to which the diazo-group is attached. When the positivity is very great, as in 2-nitronaphthalene-1-diazonium sulphate, replacement of the diazo-group by hydrogen occurs and a yield of 85% of 2-nitronaphthalene has been obtained. Gradations of positivity are well exemplified in the decomposition of the diazonium salts from substituted nitronaphthylamines with resulting variations of the predominant product, namely, symmetrical azo-compound (minimum positivity), dinaphthyl (medium positivity), and nitronaphthalene (maximum positivity). The mechanisms of the various reactions are discussed.

THE chief types of reaction to be expected from the decomposition of diazotised amines in sulphuric acid solution by cuprous hydroxide are: (1) Replacement of the diazo-group by hydrogen; (2) production of a diaryl; (3) formation of a symmetrical azo-compound; (4) the competing reaction of anionoid water to form a phenol. The formation of an arylhydrazine seems to be excluded owing to the presence of copper sulphate. All the types may occur simultaneously, as in the decomposition of 4-nitronaphthalene-1-diazonium sulphate.

The prevailing type of decomposition in any one case appears to be related to the degree of positivity of the carbon atom to which the diazo-group is attached (cf. also Hodgson, Birtwell, and Walker, J., 1941, 770). Gradations of positivity are well exemplified in the diazonium salts of substituted naphthylamines (see Table), where replacement of the diazo-group is greatest for maximum positivity as in 2-nitro-1-naphthylamine; formation of symmetrical azo-compound predominates when the positivity is relatively much smaller, as in diazotised 5-nitro-1-naphthylamine and the monochloronaphthylamines; and dinaphthyl formation occurs with intermediate values, as in 8-nitro-1- and 1-nitro-2-naphthylamines. α-Naphthylamine gave small

amounts of naphthalene and naphthol together with a tar which could not be further resolved. From 2-nitro-1-naphthylamine, a yield of 85% of 2-nitronaphthalene has been obtained.

The experimental data recorded favour the non-ionic theory of decomposition advanced by Grieve and Hey (J., 1934, 1797) and Waters (J., 1937, 2007; 1938, 843, 1077). In all the reactions now described, the cuprous hydroxide can only function as a reducing agent and not as a catalytic substance, since it dissolves in the aqueous sulphuric acid to become cupric sulphate with electron-release to the diazonium salt. The acceptance of this electron by the diazonium group can involve either (*a*) its scission from the aryl carbon atom as a nitrogen molecule, $:N\equiv N:$, thereby leaving an aryl radical, $\rangle C\cdot$, which can combine with another to form a diaryl, or (*b*) its rearrangement with formation of a diazo-radical $\rangle C-\dot{N}=\dot{N}\cdot$, which can then combine with an aryl radical (*a*) previously formed to give a symmetrical azo-compound $\rangle C-\dot{N}=\dot{N}=C\langle$. Alternatively the diazonium radieal may be formed from the diazo-component of the system,

$$\rangle C-\overset{\oplus}{N}\equiv N: \rightleftharpoons \rangle \overset{\delta+}{C}-N=\overset{\delta+}{N}-\overset{\delta-}{SO_4}H \text{ (see later).}$$

The formation of such a diazo-radical (*b*) and its subsequent combination with an aryl radical (*a*) will depend upon the electron restraint exercised by the substituent group or groups, *i.e.*, upon the degree of positivity of the carbon atom. Where this is great, as in diazotised 2-nitro- and 2 : 4-dinitro-naphthylamine, it is doubtful whether diazo-radical (*b*) is formed at all, since azo-formation has never been observed. Similarly for a somewhat lower though still high degree of positivity as in 8-nitro- and 2-nitro-1-naphthylamine the formation of (*b*) is also doubtful, and in both cases the diazo-group is probably kept in the diazonium structure by the powerful inductive ($-I$) effects of the substituents. In these compounds also, the aryl radicals formed after evolution of the nitrogen have their odd electron so restrained that in the former case only nascent hydrogen will form a pair with it, whereas with slightly less restraint the radicals (*a*) can combine. On the other hand, when the electron restraint is small or even reversed, the diazo-radical (*b*) can exist for a sufficient period to unite with radical (*a*). The positivity in 2-nitronaphthalene-1-diazonium sulphate is found experimentally to be greater than that in 1-nitronaphthalene-2-diazonium sulphate; this must be due to the unrestricted negative ($-I$) inductive effect of the second nucleus in the 2-nitro-compound (cf. Hodgson and Elliott, J., 1935, 1850; *J. Soc. Dyers and Col.*, 1938, **54**, 264).

Saunders ("The Aromatic Diazo-Compounds," 1936, p. 149) suggests that azo-compounds are probably formed during the decomposition of diazo-compounds "by a process exactly analogous to the coupling reaction, the loss of a diazo-group in one nucleus leaving a charged pole equivalent to that para to the hydroxyl group in a phenol, and to this an undecomposed diazo-molecule attaches itself." Such an ionic point of view is invalidated by the fact of diaryl or dinaphthyl formation in certain circumstances, particularly when a nitro-group is present. Such a group should promote the formation of the negative ion (see above), and thereby prevent diaryl (or dinaphthyl) formation, which requires the combination of free radicals. Further, the negative-ion theory demands the replacement of the diazo-group by the hydrogen ion and by positive chlorine in the Sandmeyer reaction, whereas actually the reducing agent supplies atomic (nascent) hydrogen and the cuprous chloride complex supplies either neutral or negative chlorine, none of which would combine with negative carbon.

In the benzene series, azo-formation is predominant throughout, and with diazotised *o*- and *p*-nitroaniline, where no diaryl formation has been observed, the results are in striking contrast to those of Niementowski (*Ber.*, 1901, **34**, 3325) and Ullmann and Forgan (*ibid.*, p. 3802), who, by using copper bronze or even copper chloride in hydrochloric acid solution, obtained considerable yields of 2 : 2′-dinitrodiphenyl from diazotised *o*-nitroaniline. When water is present in minimum amount, diaryl formation is completely suppressed (Hodgson and Walker, J., 1933, 1620). In the benzene series, notwithstanding the presence of the nitro-group, the significant carbon atom is much less positive than that in the naphthalene series owing to the greater electronic mobility in the benzene nucleus for relief of electronic strain. From diazotised *m*-nitroaniline, both diaryl and azo-compounds were obtained, and this would indicate a more even distribution of diazonium and diazo-forms in the equilibrium mixture. The nature and the concentration of the acid are thus important factors in the type of reaction favoured.

The yields of the various products are almost independent of the mode of treatment by the cuprous hydroxide, *i.e.*, whether the diazo-solution is added to it or vice versa.

In the course of this work, the experiments of Scholl, Seer, Weitzenböck, and Ertl (*Monatsh.*, 1921, **42**, 405) were confirmed, *viz.*, the formation of 5 : 5′-dinitro-1 : 1′-dinaphthyl by the action of copper on 1-iodo-5-nitronaphthalene. This observation is definitely opposed to the generalisation of Chudožilov (*Chem. Listy*, 1925, **19**, 187; cf. also Cumming and Howie, J., 1931, 3176) with respect to the unique homonuclear activity of the iodonitronaphthalenes, as also is the preparation of 8 : 8′-dinitro-1 : 1′-dinaphthyl by the action of copper on 1-iodo-8-nitronaphthalene (Hodgson and Crook, J., 1937, 571).

1 : 2-, 2 : 1-, and 1 : 4-Chloronaphthylamines give colour reactions with ferric chloride by which they may be distinguished. 2-Chloro-1-naphthylamine is much more steam-volatile than 1-chloro-2-naphthylamine.

Experimental.

Preparation of the Chloronaphthylamines.—Reduction of the chloronitronaphthalenes by stannous chloride in concentrated hydrochloric acid, by iron and acetic acid, or by West's method (J., 1925, **127**, 494) gave very similar yields (80—90%).

Steam-volatility of the Chloronaphthylamines and their Colours with Aqueous Ferric Chloride.—2-Chloro-1-naphthylamine: 3·9 g. per l. of distillate; orange-brown. 1-Chloro-2-naphthylamine: 1·7 g. per l.; greyish-violet (β-naphthylamine gave a brown colour). 4-Chloro-1-naphthylamine: 1·6 g. per l.; blue (α-naphthylamine gave a deep blue).

Decomposition of Diazonium Sulphates by Cuprous Hydroxide.—Preparation of the cuprous hydroxide. A well-stirred solution of cuprous chloride (20 g.) in hydrochloric acid (75 c.c., *d* 1·16), was treated gradually at 0° with 20% aqueous sodium hydroxide until it was just alkaline to litmus. After 30 minutes' stirring, the cuprous hydroxide was washed by decantation until free from chloride and alkali and suspended in about 100 c.c. of water (the minimum for efficient stirring during decomposition).

Preparation of the diazo-solutions. These were made either directly, *e.g.*, the suspension of fine crystals obtained from 5-nitro-1-naphthylamine (2 g.), sulphuric acid (10 c.c., *d* 1·84), and water (40 c.c.) was diazotised with sodium nitrite at 5—10°, or by Hodgson and Walker's method (J., 1933, 1620).

Decomposition. The diazo-solution was stirred at room temperature into the cuprous hydroxide suspension; the temperature rose to 28—30° and nitrogen was evolved. The mixtures were kept until coupling with alkaline β-naphthol no longer occurred. In the cases where the phenols or naphthols were not steam-volatile, the precipitates were filtered off and extracted with aqueous ammonia, and the residues steam-distilled; in others, the reaction mixtures were steam-distilled without previous treatment.

2 : 2′-*Dichloro*-1 : 1′-*azonaphthalene*, was prepared for comparison by direct diazotisation of 2-chloro-1-naphthylamine (5 g.) in hydrochloric acid (50 c.c., *d* 1·16) and water (20 c.c.), destruction of the mineral acid by sodium acetate crystals, and immediate addition of crystallised sodium sulphite (10 g.) in water (50 c.c.). The mixture was kept at room temperature for 30 minutes, heated to 60°, and cooled. The azonaphthalene crystallised from alcohol in red plates, m. p. 173—174° (Found: N, 8·0; Cl, 20·1. $C_{20}H_{12}N_2Cl_2$ requires N, 8·0; Cl, 20·2%), which gave a blue colour with concentrated sulphuric acid.

1 : 1′-*Dichloro*-2 : 2′-*azonaphthalene*, similarly prepared from 1-chloro-2-naphthylamine, crystallised from alcohol in orange-yellow plates, m. p. 170—171° (Found: N, 8·1; Cl, 20·0%), which gave a red colour with concentrated sulphuric acid.

4 : 4′-Dichloro-1 : 1′-azonaphthalene, prepared from 4-chloro-1-naphthylamine, crystallised from benzene or glacial acetic acid in small reddish-brown needles, m. p. 262—263° (Found: N, 8·2; Cl, 20·2%), which gave an ultramarine-blue colour with concentrated sulphuric acid.

Reactions of 5-Nitro-1-naphthalenediazonium Sulphate.—(a) *With copper paste.* The fine suspension obtained by chilling a solution of 5-nitro-1-naphthylamine (3·2 g.) in boiling sulphuric acid (20 c.c., *d* 1·84) and water (200 c.c.) was diazotised with sodium nitrite (2 g. in 10 c.c. of water). After 1 hour the liquid was filtered, nitrous acid destroyed by urea, and copper paste [freshly prepared from hot crystallised copper sulphate (30 g.) in water (200 c.c.) and zinc dust (10 g.) and washed by decantation] added. Nitrogen was evolved immediately, and the decomposition was completed on the water-bath. Steam-distillation removed 1-nitronaphthalene (0·2 g.); the residue consisted of a very small amount of 5-nitro-1-naphthol (extracted by alkali) and 5 : 5′-dinitro-1 : 1′-azonaphthalene (0·9 g.), which was extracted by boiling benzene.

(b) *With copper bronze* (5 g.). The products were 1-nitronaphthalene (0·2 g.), 5 : 5′-dinitro-1 : 1′-azonaphthalene (1·4 g.), and 5-nitro-1-naphthol (small amount, not estimated).

(c) *With copper bronze* (5 g.) *and ethyl alcohol* (50 c.c.). The diazo-solution (a) yielded α-nitronaphthalene (1·05 g.); the other products were not identified.

(d) *With cuprous hydroxide.* See Table.

Table of Individual Decompositions.

Amine diazotised (g.).	Azo-compound, g.	Azo-compound, %	Phenol or naphthol, g.	Phenol or naphthol, %	Deaminated product, g.	Deaminated product, %	Remarks.
Aniline (3·4)	1·1	33·0	0·9	20·5	0·8	27·5	
o-Chloroaniline (2·2)	1·75	80·0	Trace	—	Trace	—	
m-Chloroaniline (3·2)	None	—	0·9	28·0	,,	—	1 G. of *mm*′-dichlorodiphenyl (35%)
p-Chloroaniline (2·2)	1·5	70·0	0·4	31·0	,,	—	
o-Nitroaniline (3·4)	1·2	35·0	Trace	—	1·2	39·5	
m-Nitroaniline (3·4)	See remarks		,,	—	0·5	13·0 →	Fractional crystallisation from a mixture of equal parts of methyl alcohol and glacial acetic acid indicated the bulk of the product to be *mm*′-dinitroazobenzene and *mm*′-dinitrodiphenyl
p-Nitroaniline (3·4)	1·2	35·0	0·45	13·0	0·25	8·0	
β-Naphthylamine (3·6)	1·9	54·0	Trace	—	1·1	34·0	
2-Chloro-1-naphthylamine (2·2)	1·4	65·0	,,	—	0·5	25·0	
1-Chloro-2-naphthylamine (2·2)	1·9	87·5	,,	—	Trace	—	
4-Chloro-1-naphthylamine (2·2)	1·7	78·3	,,	—	,,	—	
2-Nitro-1-naphthylamine (2·3)	None	—	,,	—	1·8	85·0	
1-Nitro-2-naphthylamine (2·3)	,,	—	,,	—	0·2	10·0	1·35 G. of 1 : 1′-dinitro-2 : 2′-dinaphthyl
4-Nitro-1-naphthylamine (2·3)	Trace	—	0·75	32·5	0·65	31·0	
5-Nitro-1-naphthylamine (2·3)	0·8	40·5	0·3	15·0	0·8	42·0	

5 : 5′-*Dinitro*-1 : 1′-*azonaphthalene*, which was also prepared by the sulphite method described above, crystallised from boiling nitrobenzene in yellowish-brown needles, m. p. 322—323° (Found: N, 15·2. $C_{20}H_{12}O_4N_4$ requires N, 15·1%), which were obtained in orange-yellow needles, m. p. 322—323°, by sublimation. It was sparingly soluble in boiling alcohol, glacial acetic acid, and benzene; the colour with concentrated sulphuric acid was reddish-violet, which changed to yellow on heating.

5 : 5′-*Dinitro*-1 : 1′-*dinaphthyl.*—5-Iodo-1-nitronaphthalene (3 g.) [purified by vacuum sublimation and by crystallisation from alcohol; small yellow needles, m. p. 165° (Scholl, Seer, Weitzenböck, and Ertl, *loc. cit.*, give m. p. 164°)] was heated with copper bronze at 220—230° for 90 minutes. The material extracted by boiling benzene was recovered and extracted repeatedly with ether to remove unchanged 5-iodo-1-nitronaphthalene. The residual 5 : 5′-dinitro-1 : 1′-dinaphthyl (0·95 g.) crystallised from glacial acetic acid (charcoal) in light brown plates, m. p. 228—229° (Scholl, Seer, Weitzenböck, and Ertl give m. p. 228—228·5°) (Found: N, 8·2. Calc.: N, 8·1%).

The authors are indebted to Mr. J. Habeshaw for the preparation of 2 : 2′-dichloro-1 : 1′-azonaphthalene and 1 : 1′-dichloro-2 : 2′-azonaphthalene, and to Imperial Chemical Industries (Dyestuffs) Ltd., for various gifts.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, August 1st*, 1942.]

163. *The Influence of* p-*Substituents on the Decomposition of Zinc Chloride Double Salts of Diazonium Chlorides by Acetic Anhydride.*

By Herbert H. Hodgson and Clifford K. Foster.

Five double salts of *p*-substituted diazonium chlorides and zinc chloride were decomposed by acetic anhydride with simultaneous replacement of the diazo-group mainly by acetoxyl or chlorine, the former predominating. The comparative influence of the *p*-substituents towards acetoxyl replacement is in the decreasing order of the negative ($-I$) effects, *viz.*, Cl>OMe>Me. The special case of the hydroxyl group is discussed.

Five typical double salts of diazonium chlorides and zinc chloride have been decomposed by acetic anhydride, which gives rise mainly to two simultaneous reactions: (1) External replacement of the diazo-group by the acetoxy-group, due to nucleophilic attack by the pronounced anionoid acetic anhydride-oxygen at the kationoid carbon atom to which the diazo-group is attached (cf. also Hodgson and Foster, this vol., p. 30). (2) Replacement of the diazo-group by attack of the less anionoid chlorine of the zinc chloride complex under the anhydrous conditions of the reaction medium at the same carbon atom (cf. Hodgson, Birtwell, and Walker, J., 1941, 770).

In the cases of the double salts with diazotised β-naphthylamine and *p*-aminophenol, β-naphthyl acetate and *p*-diacetylquinol were readily isolated in yields of 48% and 70% respectively; but for purposes of quantitative comparison the corresponding acetoxy-compounds afforded by *p*-toluidine, *p*-chloroaniline, and *p*-anisidine were first subjected to alkaline hydrolysis, after which the *p*-cresol, *p*-chlorophenol, and *p*-hydroxyanisole respectively formed were readily isolated and estimated. In all five cases reaction (1) was appreciably greater than (2), and the combined yields of acetoxy- and chloro-products were of the order of 80%. When the yields of phenols above are calculated as amounts of acetoxy-compound formed per g.-mol. of zinc chloride double salt taken, the decreasing order is: *p*-hydroxy (21·3) > *p*-chloro (16·3) > *p*-methoxy (13·0) > *p*-methyl (11·6), and except for the first member this sequence is the order of the decreasing negative ($-I$) inductive effects of the *p*-substituents, *i.e.*, in the order of decreasing positivity of the carbon atom to which the diazo-group is attached, as would be expected. Since the product isolated from the reaction between the zinc chloride double salt of *p*-hydroxybenzenediazonium chloride and acetic anhydride is diacetylquinol, it is a reasonable assumption that, under the favourable conditions present for acetylation, the double salt becomes acetylated prior to decomposition at 110°, and that it is the acetoxy-group which is exerting the observed powerful ($-I$) inductive effect on the carbon atom. Alternatively, the phenolic group, if not acetylated, has nevertheless exercised such an electron-attracting effect that the oxygen must be in a partial oxonium (positive) condition due to two-point attack of the polarised acetic anhydride on the polarised phenolic group (cf. the analogous decomposition of *p*-hydroxybenzenediazonium salts by alcohols; Hodgson and Foster, J., 1940, 1150). In the case of the double salt decompositions by phenol (Hodgson and Foster, this vol., p. 581), where chlorine substitution is the predominant reaction, the special effect of the phenolic group found above is absent.

Experimental.

The various double salts decomposed, $(ArN_2)_2ZnCl_4$, are referred to below by the initial amine employed.

β-Naphthylamine.—The double compound (13·6 g.) (equivalent to 10 g. of naphthalene-β-diazonium chloride) was added portionwise to acetic anhydride (50 c.c.) at 60°; the heat of reaction raised the temperature to 90°, nitrogen was evolved briskly, and the temperature was maintained at 90—95° by the rate of addition. When reaction was completed, the mixture was diluted with glacial acetic acid (50 c.c.), poured into water, and fractionally steam-distilled; 2-chloronaphthalene [2·0 g. (23·5% yield), m. p. 56°] passed over first, and was followed much more slowly by 2-naphthyl acetate [3·4 g. (35% yield), m. p. after recrystallisation from aqueous ethyl alcohol, 70°]; β-naphthol (1 g., 13·3% yield) was also collected and was doubtless formed by hydrolysis of the acetate during the prolonged steam-distillation; 0·7 g. of non-volatile tar remained in the steam flask.

p-*Toluidine.*—The double compound (14·4 g.) was added gradually to acetic anhydride (50 c.c.) at 90°, at which temperature reaction occurred, and after its completion, the mixture was diluted with glacial acetic acid (50 c.c.), stirred into cold aqueous sodium hydroxide until alkaline, boiled for 20 minutes, and steam-distilled; *p*-chlorotoluene then passed over (2·7 g., 33·4% yield). When the flask liquor was just acidified with sulphuric acid and steam-distilled, *p*-cresol (2·7 g., 38·6% yield), formed by the above hydrolysis of the initially formed *p*-tolyl acetate, passed over.

p-*Chloroaniline.*—The double compound (14·0 g.) was brought into reaction as above. On steam distillation of the alkaline hydrolysis mixture, *p*-dichlorobenzene (2·6 g., 31% yield) first passed over, and then much more slowly, traces of an unidentified, pale yellow substance which was not *pp'*-dichlorodiphenyl. On steam-distillation of the acidified flask liquor and treatment of the distillate with bromine water, 4-chloro-2 : 6-dibromophenol (8 g., corresponding to a 49% yield of *p*-chlorophenol in the original reaction) was obtained.

p-*Anisidine.*—With decomposition details as for *p*-toluidine, 14 g. of the double salt being used, evolution of nitrogen did not occur until a temperature of 125—130° was attained. On steam-distillation of the alkaline hydrolysis liquor, *p*-chloroanisole (2·4 g., 29% yield) passed over. The flask liquor was then treated with excess of methyl sulphate, quinol dimethyl ether being obtained (3·2 g., corresponding to a 39% yield of *p*-hydroxyanisole).

p-*Aminophenol.*—With 14·4 g. of double salt and decomposition as above by acetic anhydride (75 c.c.), a temperature of *ca.* 110° was required before evolution of nitrogen commenced. At the end of the reaction, glacial acetic acid (75 c.c.) was added, and the cooled solution poured into ice-water (500 c.c.); diacetylquinol was obtained (8·7 g., 70% yield), m. p. after recrystallisation from aqueous ethyl alcohol and mixed m. p. with an authentic specimen, 123°. The filtrate

was made alkaline with sodium hydroxide, and the mixture refluxed for 20 minutes, made acid, and steam-distilled; *p*-chlorophenol passed over and was estimated as 4-chloro-2 : 6-dibromophenol (3·8 g., corresponding to a yield of 18·8% of *p*-chlorophenol).

The authors thank Imperial Chemical Industries (Dyestuffs) Ltd. for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, September 22nd*, 1942.]

---

164. *The Action of Cuprous Oxide on Diazotised Amines in Ethyl-alcoholic Acid Solution.*

By HERBERT H. HODGSON and HAROLD S. TURNER.

Amines can be efficiently deaminated when their diazonium salts in glacial acetic–concentrated sulphuric acid solution are decomposed by a suspension of cuprous oxide in ethyl alcohol. The method appears to be of general application.

HODGSON and MARSDEN'S method (J., 1940, 207) for the replacement of a diazo-group by hydrogen is of general application and almost quantitative, but it involves the preliminary isolation of a stabilised salt of the diazotised amine with a naphthalenedisulphonic acid or an acid such as oxy-Tobias acid. This preparation may be easy or difficult, and the method now described deals with the diazotised amine *in situ*. It is based on the reducing action of cuprous oxide and ethyl alcohol in conjunction with the diazotisation of the amine by Hodgson and Walker's method (J., 1933, 1620). Ruggli, Knapp, Merz, and Zimmermann (*Helv. Chim. Acta*, 1929, **12**, 1034) have used cuprous oxide and alcohol for the reduction of 6-nitro-1-diazo-2-naphthol-4-sulphonic acid to 6-nitro-2-naphthol-4-sulphonic acid.

The efficiency of the ethyl alcohol–cuprous oxide combination for the deamination of certain derivatives of 5-nitro-1-naphthylamine (Hodgson and Turner, this vol., p. 723) indicated that the method might be of general application, and the data now included (see Table) show this to be the case. Excellent yields of deaminated products have been obtained from nitroamines and aminoanthraquinones, and good yields from amines having less pronouncedly kationoid substituents. It appears that the positivity of the carbon atom to which the diazo-group is attached is the dominant factor in the decomposition; *e.g.*, this atom in 2-nitro-1-naphthylamine (79% yield of 2-nitronaphthalene) is somewhat more positive than that in 1-nitro-2-naphthylamine (70% yield of 1-nitronaphthalene), as would be expected on the assumption of a negative inductive ($-I$) effect of the second nucleus (Hodgson and Elliot, J., 1935, 1850).

In the method the amine is diazotised in glacial acetic–nitrosylsulphuric acid (Hodgson and Walker, *loc. cit.*), and the solution run into a suspension of cuprous oxide in ethyl alcohol; the diazonium group is smoothly replaced by hydrogen, the deaminated product is obtained in a high state of purity and unaccompanied by azo-compounds, and diaryl or dinaphthyl production is negligible (cf. Ullman and Forgan, *Ber.*, 1901, **34**, 3803). The yields are not appreciably affected by the state of the cuprous oxide, provided it is very finely divided; the commercial variety, the yellow hydrated form, and the red powder obtained by the reduction of alkaline cupric solutions have all been found suitable. The function of the cuprous oxide may be both catalytic and direct, since it is almost completely dissolved in the reaction mixture as highly reactive cuprous sulphate. Subsequent reaction appears to be the formation of " nascent " copper, by which the decomposition of the diazonium group would be considerably facilitated; the alcohol, by its oxidation to aldehyde, participates in the reduction process, and its activity is doubtless increased by the nascent copper present (cf. the formation of aldehydes from alcohols by copper).

Although the yields of deaminated product are somewhat lower in many cases than those obtained by the Hodgson–Marsden procedure (*loc. cit.*), the present method is very convenient (especially with the less basic and the more difficultly diazotisable amines), since it is easy and rapid and is particularly useful for small quantities of amine (0·1—0·5 g.).

EXPERIMENTAL.

Procedure.—A solution of the amine (1/20 g.-mol.) in glacial acetic acid (80 c.c.) was added, below 20°, to a solution of sodium nitrite (4·5 g.) in sulphuric acid (30 c.c., *d* 1·84); after 30 minutes, the mixture was run into a vigorously stirred suspension of finely divided cuprous oxide (14 g.) in absolute ethyl alcohol (120 c.c.) during *ca.* 30 minutes. Evolution of nitrogen began forthwith, the temperature rose to 50—70°, and the reaction was complete in less than 5 minutes.

Isolation of the Products.—(1) For steam-volatile compounds, the reaction mixture was diluted with an equal volume of water and steam-distilled.

(2) For compounds readily soluble in alcohol, the liquid was filtered, the residue washed with boiling alcohol (50—100 c.c.), and the combined filtrates diluted gradually with water; the precipitate was pure after recrystallisation.

(3) For compounds non-volatile in steam and moderately soluble or insoluble in alcohol, the mixture was diluted with water (1·5 l.), and the precipitate collected, washed, dried, and extracted with ethylene dichloride or chloroform. The extract afforded the product in a high state of purity.

The yields recorded in the table are minimum yields of pure products, and can usually be increased by 3—10% by slight changes in technique, determined by trial and error. The substitution of formic for acetic acid (equal vols.) in the diazotisation usually increased the yield by *ca.* 5%.

Table.

Except where otherwise stated, the "oxide" mentioned is the hydrated product precipitated by alkali from cuprous chloride solution. The yellow solid was washed with water, alcohol, and ether, and vacuum-dried.

Amine.	G.-mol.	Acetic acid, c.c.	Sodium nitrite, g.	Sulphuric acid, c.c.	Cuprous oxide, g.	Alcohol, c.c.	Method of isolation of product.	Final temp.	Yield, %
p-Toluidine	0·1	40	9	60	28 [1]	200	Dilution, separation of toluene layer, distillation.	Below 40°	45
o-Nitroaniline	0·05	40	4·5	30	14	120	(1)	60	89
m-Nitraniline	0·05	40	4·5	30	14	120	(1)	60	78
p-Nitroaniline	0·05	40	4·5	30	19	120	(1)	65	97
Anthranilic acid	0·05	40	4·5	30	14	120	(2) [2]	75	65
2 : 5-Dichloroaniline	0·05	20	4·5	30	14	120	(2) followed by (1)	62	57
3 : 5-Dinitro-*p*-toluidine	0·025	40	2·5	20	7 [3]	60	(1)	55	40
Benzidine	0·05	40	9	60	26	200	(1)	68	49 [4]
β-Naphthylamine	0·05	40	4·5 [5]	30	14	120	(1)	50	60
1-Nitro-2-naphthylamine	0·05	50	4·5	30	10 [3]	120	(2) followed by (1)	75	70
2-Nitro-1-naphthylamine	0·05	40	4·5	30	12 [3]	120	(2) followed by (1)	75	79
4-Chloro-2-nitro-1-naphthylamine	0·025	80	2·5	20	10	60	(2)	60	94
2-Iodo-4-nitro-1-naphthylamine	0·025	40	2·5	20	10	60	(2)	70	80
2 : 4-Dinitro-1-naphthylamine	0·05	70	4·5	Total 68	14 [6]	150	(3)	60	65
1-Aminoanthraquinone	0·05	80	4·5	30	14	120	(3)	75	75
2-Aminoanthraquinone	0·05	80	4·5	30	14 [1]	170	(3)	72	70

[1] Commercial oxide used. [2] The product was a mixture of benzoic acid and ethyl benzoate. After dilution, the aqueous solution was ether-extracted. Aqueous sodium hydroxide removed the acid—reprecipitated by mineral acid. Distillation of the residual ether gave the ester (2·0 c.c., b. p. 215°). [3] Precipitated red cuprous oxide used. [4] The hypophosphite method (Mai, *Ber.*, 1902, **35**, 162) gives a 60% yield of diphenyl from benzidine. [5] Excess of nitrous acid removed by urea before deamination. [6] Commercial oxide used. 2 : 4-Dinitro-*p*-toluenesulphon-1-naphthalide was hydrolysed by sulphuric acid (*d* 1·84) and diazotised *in situ* by the inverted method.

The authors thank Imperial Chemical Industries (Dyestuffs) Ltd. for various gifts.

Technical College, Huddersfield. [*Received, September 22nd*, 1942.]

165. *Studies on Agar-agar. Part III. Isolation of Hepta-acetyl* dl-*Galactose from* 3 : 6-*Anhydro*-β-*methyl*-d-*galactoside.*

By T. L. Cottrell and E. G. V. Percival.

It is shown that 3 : 6-anhydro-β-methyl-*d*-galactoside yields hepta-acetyl *dl*-galactose on treatment with acetic anhydride and sulphuric acid. The conclusion is drawn that the hepta-acetyl *dl*-galactose isolated in the same manner from agar by Pirie arises by a similar reaction with the 3 : 6-anhydro-*l*-galactose units.

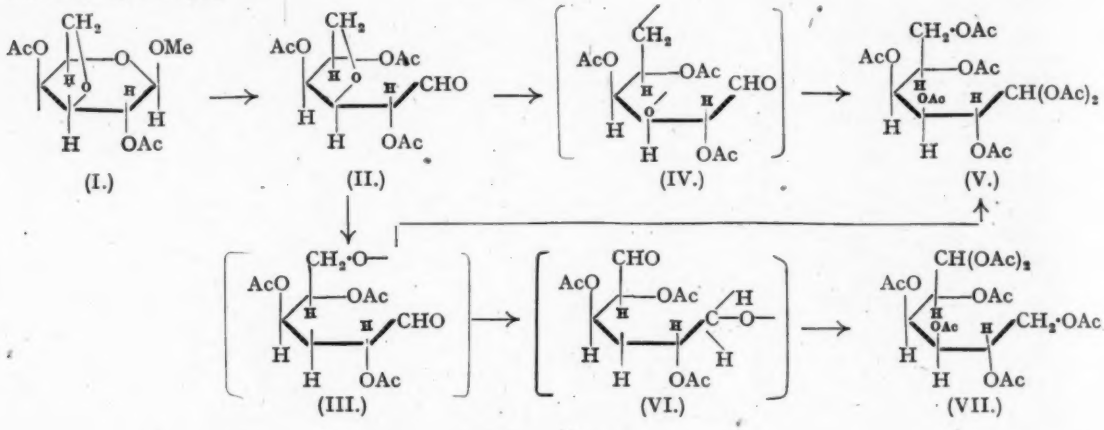
The isolation of hepta-acetyl *dl*-galactose from agar by treatment with acetic anhydride and sulphuric acid by Pirie (*Biochem. J.*, **1936**, **30**, 369) was at first thought to indicate that galactose in the aldehydo-form was present in the molecule. Freudenberg and Soff (*Ber.*, **1937**, **70**, 264) showed, however, that aldehydo-*d*-glucose hepta-acetate could be obtained under similar conditions from glucopyranose derivatives, and, despite the subsequent proof of the presence of *l*-galactose in agar as 3 : 6-anhydro-*l*-galactose (Part II, J., 1939, 1844; Hands and Peat, *Chem. and Ind.*, **1938**, **57**, 1937), the observations of Micheel, Ruhkopf, and Suckfüll (*Ber.*, **1935**, **68**, 1523) that hepta-acetyl *dl*-galactose could be prepared from tetra-acetyl *d*-galactose 6-iodohydrin, made it uncertain that the hepta-acetate in question came from the *l*-galactose fragment in agar.

Jones and Peat (this vol., p. 225) have suggested that the isolation of the *dl*-galactose hepta-acetate can be accounted for by the acid hydrolysis of a sulphuric ester residue attached to the *l*-galactose residue to give *l*-galactose and this with the *d*-galactose already present is converted into hepta-acetyl *dl*-galactose under the experimental conditions.

We have now proved that 3 : 6-anhydro-β-methyl-*d*-galactoside, when treated with acetic anhydride and sulphuric acid, gives hepta-acetyl *dl*-galactose and we therefore consider that in the case of agar the hepta-acetyl *dl*-galactose is formed exclusively from the 3 : 6-anhydro-*l*-galactose residues which are linked to other residues by 1 : 4-linkages. This is supported by the fact that the yield of hepta-acetyl *dl*-galactose (10—20% by weight) agrees with the estimate of the proportion of 3 : 6-anhydro-*l*-galactose in agar. Pirie (*loc. cit.*) was unsuccessful in attempts to obtain hepta-acetyl *d*-galactose from *d*-galactose, β-penta-acetyl *d*-galactopyranose and β-penta-acetyl *d*-galactofuranose under the same conditions.

In the experiment under review it is reasonable to suppose that 3 : 6-anhydro-β-methyl-*d*-galactoside is transformed into hepta-acetyl *dl*-galactose through the following stages, in which it may be assumed that 2 : 4-diacetyl 3 : 6-anhydro-β-methylgalactoside (I) is first formed, and is hydrolysed and acetylated to give

2 : 4 : 5-triacetyl 3 : 6-anhydro-aldehydo-*d*-galactose (II). Cleavage of the 3 : 6-anhydro-ring may then give either of the transient forms (III) or (IV) in the same way as the rupture of an ethylene oxide ring with alkali (Peat, *Ann. Reports*, 1939, 262). (IV) then yields with the acetic anhydride hepta-acetyl *d*-galactose (V). The formation of an equivalent amount of hepta-acetyl *l*-galactose (VII) may be supposed to result from the formation of (VI) from (III) by the migration of a hydrogen atom, C_1 and C_6 being in close proximity in space, followed by acetylation to yield (VII). Since (III) could also yield (V) on acetylation, an alternative explanation would be that (III) is the product of the rupture of the anhydride ring and that an equilibrium exists between (III) and (VI).



Experimental.

3 : 6-Anhydro-β-methyl-*d*-galactoside (m. p. 118°, $[\alpha]_D$ −113°, 4 g.) was treated for 54 hours at 37° with acetic anhydride (18 c.c.) and sulphuric acid (3 c.c.). The mixture was then poured on ice and, after addition of sodium acetate (10 g.), extracted several times with chloroform; the extract was washed with sodium bicarbonate solution and water, dried with sodium sulphate, and evaporated to a syrup, which crystallised on solution in alcohol and treatment with a nucleus of hepta-acetyl *dl*-galactose. The crystalline material (0·5 g.) so obtained had m. p. 126°, not depressed by hepta-acetyl *dl*-galactose (m. p. 126°) isolated from agar by Pirie's method (*loc. cit.*). The m. p. (132°) recorded by Pirie could not be reached after six recrystallisations. $[\alpha]_D^{18°}$ +0° in chloroform (*c*, 3·0) (Found: C, 48·2; H, 5·8; CH_3·CO, 60·1. Calc. for $C_{20}H_{28}O_{14}$: C, 48·8; H, 5·7; CH_3·CO, 61·1%).

[With T. G. H. Thomson.] Washed agar (60 g.), treated according to Pirie for 26 hours at 38°, gave 3·0 g. of hepta-acetyl *dl*-galactose and for 33 hours 4·8 g.; none was isolated after 2 hours' acetolysis.

Thanks are expressed to Mr. R. B. Duff, B.Sc., for the preparation of 3 : 6-anhydro-β-methylgalactoside, and to Imperial Chemical Industries, Ltd., and the Earl of Moray Endowment for grants.

King's Buildings, University of Edinburgh. [*Received, October 22nd*, 1942.]

---

166. *Studies on Agar-agar. Part IV.*

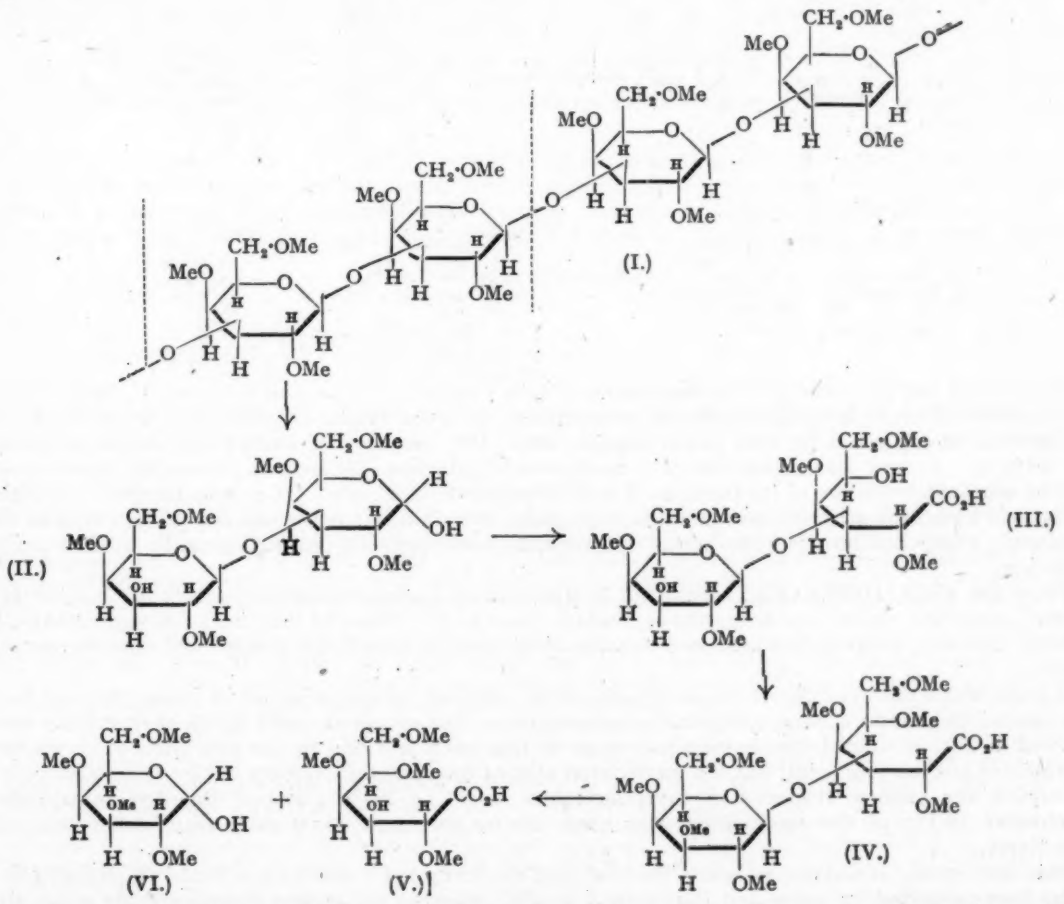
By E. G. V. Percival and T. G. H. Thomson.

By the acetolysis of methylated agar, followed by oxidation, a mixture of disaccharide esters was obtained from which on hydrolysis and suitable treatment tetramethyl *d*-galactopyranose anilide was isolated together with a mixture of methylated acids. It was concluded that the main acid product was 2 : 4 : 5 : 6-*tetramethyl* d-*galactonic acid* and an accompanying crystalline acid was shown to be 2 : 5-*dimethyl* 3 : 6-*anhydro*-l-*galactonic acid*, thus proving the linkage of the 3 : 6-anhydro-*l*-galactose residues to the *d*-galactopyranose units to be at C_4 as suggested by Jones and Peat (this vol., p. 225).

The absence of a non-reducing end group of tetramethyl galactose is confirmed and evidence for the presence of dimethyl methylgalactosides in the products of hydrolysis is presented. The products obtained on heating agar at 130° with water have been studied and their relation to the agar molecule is discussed.

Haworth and Percival (J., 1931, 1342) used the method of degrading methylated starch and glycogen with acetyl bromide, followed by oxidation, to show that contiguous glucose units in these polysaccharides were pyranose. The application of this method to agar was instituted, not to decide the configuration of the *d*-galactose residues, since the isolation of 2 : 4 : 6-trimethyl galactose from methylated agar by Percival and Somerville (Part I; J., 1937, 1615) had already shown them to be pyranose and linked through C_1 and C_3, but to decide, if possible, the mode of attachment and configuration of the *l*-galactose residues which had been isolated as 2 : 4-dimethyl 3 : 6-anhydro-β-methyl-*l*-galactoside by methylation of the hydrolysis products of methylated agar (Hands and Peat, *Chem. and Ind.*, 1938, **57**, 937; Forbes and Percival, *Nature*, 1938, **142**, 797; Part II, J., 1939, 1844), although the proportion of the disaccharide containing the *l*-galactose fragment, if such could be isolated, would obviously be small because of the preponderating proportion of *d*-galactose units.

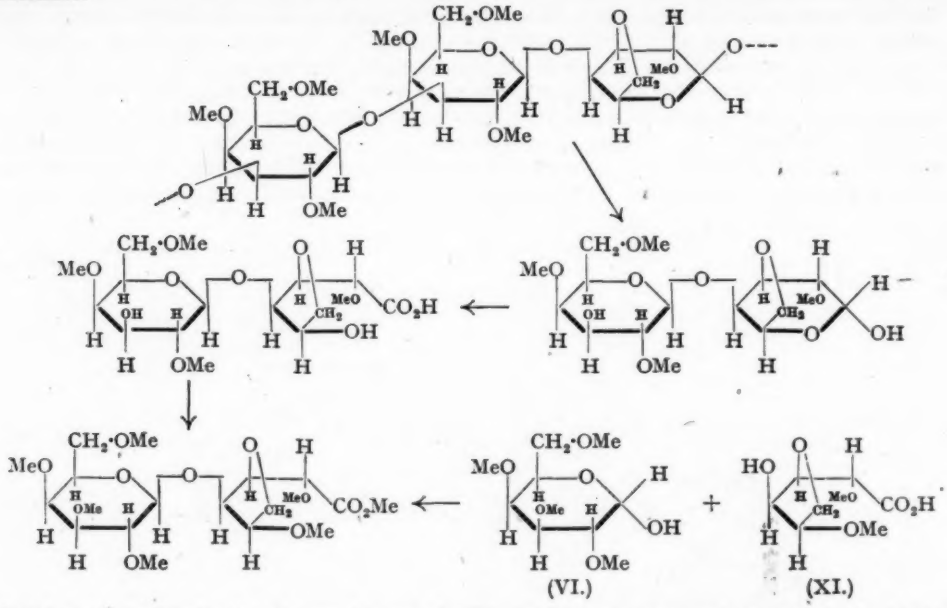
Methylated agar was degraded with acetyl bromide and the products after suitable treatment were oxidised and methylated; distillation in a high vacuum gave mainly crystalline *pentamethyl methyl*-d-*galactonate*, but a fraction was also isolated which appeared to be a mixture of methylated disaccharide esters. Hydrolysis of this disaccharide mixture yielded tetramethyl *d*-galactopyranose (VI), characterised as the anilide. On some occasions the accompanying methylated hexonic acid crystallised, but the major portion was a syrup which would not lactonise, and which was concluded to be mainly 2 : 4 : 5 : 6-tetramethyl *d*-galactonic acid (V), since the corresponding amide gave a negative Weerman test and the ester on methylation yielded crystalline pentamethyl methyl-*d*-galactonate. This evidence does not exclude the possibility that the acid was 2 : 3 : 4 : 5-tetramethyl galactonic acid, but the above interpretation is in harmony with the view that most of the *d*-galactopyranose residues are joined together by 1 : 3-linkages (I); the various stages in the analysis are represented below.



The crystalline acid (m. p. 160°, $[\alpha]_D^{18°}$ −65°) proved to be 2 : 5-*dimethyl* 3 : 6-*anhydro*-l-*galactonic acid* (XI) for the following reasons: The physical constants, apart from the sign of the rotation, closely resemble those for 2 : 4-dimethyl 3 : 6-anhydro-*d*-galactonic acid (Haworth and Smith, J., 1940, 620), but a mixed m. p. determination with the *l*-acid (m. p. 151°) showed a depression of 30°. Jones and Peat (this vol., p. 225) have isolated from methylated agar an amide which they describe as 2 : 5-dimethyl 3 : 6-anhydro-*l*-galactonamide (m. p. 173°). The above acid was also converted into an amide, m. p. 171°, which gave a negative Weerman reaction and appears to be identical with that of Jones and Peat, so the conclusions of these workers as to the mode of union of the 3 : 6-anhydro-*l*-galactose residues to the *d*-galactose units by 1 : 4-linkages are supported by our acetolysis experiments, as shown on p. 752.

In Part I (*loc. cit.*) it was pointed out that no tetramethyl *d*-galactopyranose was detectable in the hydrolysis products of methylated agar; the quantity used, however, was not sufficient to decide definitely that a non-reducing end group of *d*-galactose did not exist. Larger quantities of methylated agar have now been hydrolysed, and the original provisional conclusion confirmed. Jones and Peat (*loc. cit.*) have indeed accepted this view and made use of it to formulate a structure for agar embodying a repeating unit of nine *d*-galactopyranose residues joined by β-linkages through the 1 : 3-positions, terminated by one *l*-galactopyranose-6-sulphate residue attached by position 4, the reducing group of this residue being attached to the terminal *d*-galactopyranose unit of another similar chain. It does not appear to us, however, that this conception of the agar molecule

accords with all the facts, although, as indicated above, we agree as to the mode of union of the *l*-galactopyranose residues.



As pointed out previously, in the specimens of agar used by us (Duff and Percival, J., 1941, 830) there is no question of the hydrolysis of a sulphate group in the *l*-galactose residue to yield a 3 : 6-anhydro-ring during methylation as suggested by Peat (*Ann. Reports*, 1941, 154) because the washed agar employed contained but 0·1% S. A very small quantity of a methylated *l*-galactose (isolated as *tetramethyl* l-*galactopyranose anilide*) was detected in one of the fractions of hydrolysed methylated agar. It is probable that this originated by the acid hydrolysis of a sulphate group at some stage, since it has now been shown (E. E. Percival, Thesis, Edinburgh, 1942) that the acid hydrolysis of β-methylgalactoside sulphate proceeds normally without anhydride formation.

From the yield (11·5%) of 2 : 4-dimethyl 3 : 6-anhydro-β-methyl-*d*-galactoside recorded in Part II (*loc. cit.*) the proportion of *d*- to *l*-galactopyranose units is closer to 15 : 2 than to that of 9 : 1 as suggested by Jones and Peat (*loc. cit.*), although the precise evaluation of this ratio is admittedly difficult and must be stated with reserve.

A point which renders difficult the acceptance of the relatively simple structure of Jones and Peat (*loc. cit.*) concerns the yield of 2 : 4 : 6-trimethyl methylgalactosides. The maximum yield (65%) of crystalline material recorded in Part II admittedly may exclude some of this fraction owing to the difficulties of crystallising a substance of low melting point, but if a methylated agar of the composition proposed by Jones and Peat were hydrolysed, the yield of trimethyl methylgalactosides would be 104·8% and of dimethyl anhydromethylgalactosides 10·1% of the methylated agar used, the figures for a 15 : 2 ratio being 103% and 11·9% respectively.

This discrepancy is serious, as is also the fact that the methoxyl content for a model of methylated agar on the lines suggested by Jones and Peat should be 42%, whereas the highest recorded value is not greater than 35% for a representative sample (Jones and Peat, *loc. cit.*).

The view was expressed in Part II (*loc. cit.*) that dimethyl methylgalactosides were probably present in the fraction containing the monomethyl 3 : 6-anhydromethyl-*l*-galactosides. This is now confirmed and, although precise evaluation of the proportion is difficult owing to the failure to isolate crystalline products, the amount may be as high as the yield of dimethyl anhydromethylgalactosides. Whether one is dealing with a single dimethyl galactose, or a mixture, is uncertain, since the product was contaminated with decomposition products of the monomethyl anhydromethylgalactosides, but tetramethyl *d*-galactopyranose anilide was isolated in good yield on methylation and anilide formation, and the amorphous osazone obtained in the usual way appeared to be a monomethyl hexosazone, which would indicate substitution of methoxyl at C_2. In the absence of non-reducing end group fractions the only explanation, that appears possible in the present state of our knowledge, of the presence of dimethyl galactoses is that complete methylation of agar has not yet been achieved, although it may be remarked that the use of sodium in liquid ammonia (Part II, *loc. cit.*) failed to raise the methoxyl content of methylated agar appreciably.

The treatment of agar with water in an autoclave at 130° was shown by Takahashi and Shirahama (*J. Fac. Agr. Hokkaido Imp. Univer., Japan*, 1934, **35**, 101) to yield two distinct degradation products, hydrato-kanten δ (hereafter called " δ "), which formed a gel with water, and hydrato-kanten λ (" λ "), soluble in water. This work has now been repeated and the products " δ " and " λ " acetylated, methylated, and hydrolysed to

determine the relationship of these and more highly degraded products "δ_1" and "λ_1" to agar and to one another. Comparative determinations of molecular weight (which must not be regarded as absolute values) were made by the viscosity method and by the determination of reducing power by alkaline hypoiodite; the results are in Table I.

TABLE I.

	$[\alpha]_D$.	% OMe.	% OAc.	M_v.	M_0.	M_1.
Methylated agar	−86°	32	—	15,500	12,300	16,000
Acetylated agar	−32	—	37	29,500	16,600	—
Methylated "δ"	−82	32·4	—	7,800	6,250	8,100
Acetylated "δ"	−32·5	—	36·5	10,000	5,630	—
Acetylated "δ_1"	−32	—	38	6,000	3,400	3,300
Methylated "λ"	−86	34	—	4,500	3,600	3,400
Acetylated "λ"	−40	—	40	4,500	2,500	—
Acetylated "λ_1"	−37	—	44	2,500	1,400	1,200

M_v denotes the apparent molecular weights by the viscosity method, taking $K_m = 10^{-3}$, and are mean values (except for "λ_1"). M_0 is the apparent molecular weight calculated from M_v, the repeating unit being reckoned as $C_6H_{10}O_5$. M_1 is the apparent molecular weight calculated from the iodine number determined for the unsubstituted polysaccharide.

The chemical composition of "δ" and "λ" was investigated by methanolysis of the methylated derivatives. The trimethyl methylgalactosides were estimated in the usual way, and the proportion of 3 : 6-anhydromethyl-*l*-galactosides found by methylation and isolation of the crystalline β-methylgalactoside. The results are in Table II, and show that the products of hydrolysis of the three substances concerned are closely similar.

TABLE II.

		Agar.	"δ."	"λ."
2 : 4 : 6-Trimethyl methyl-*d*-galactosides, %		65	52	59
2 : 4-Dimethyl 3 : 6-anhydro-β-methyl-*l*-galactoside	(*a*)	8	11	9
(*a*) crystalline (*b*) estimated	(*b*)	11·5	14·9	13·3

The difference in properties of "δ" and "λ" is not explained by this analysis, so the physical differences between them and the failure to convert "δ" into "λ" must arise from some difference in arrangement at present obscure.

EXPERIMENTAL.

The Washing of Agar.—Powdered agar (B.D.H.) (10 g.; ash 3·2%, S 0·3%) was washed ten times with water (2 l. each time) during 10 days. The p_H of the first washing liquid as determined by the quinhydrone electrode was 7·0 as for the subsequent washings. The product after treatment with alcohol and ether and drying had ash 1·2%, S 0·1%. This material was acetylated to yield a product which after precipitation from chloroform solution with light petroleum had $[\alpha]_D^{18°}$ −32°. The specific rotations are determined in chloroform (*c*, 1·0) unless otherwise stated (Found: Ash, 0·4; S, 0·03; $CH_3{\cdot}CO$, 37·1%).

The Acetolysis of Methylated Agar.—Methylated agar (44 g.), prepared from agar (B.D.H.) as described in Part I (*loc. cit.*) ($[\alpha]_D^{18°}$ −86°; OMe, 32·5%), was treated in 4 g. portions in chloroform (40 c.c.) with acetyl bromide (12 c.c. in chloroform, 15 c.c.). After 7½ hours the mixtures were poured into ice-water; more chloroform was added and the chloroform solution was washed with sodium bicarbonate solution and ice-water until free from acid, and dried over sodium sulphate. Evaporation gave a yellow syrup which contained bromine and reduced Fehling's solution. The subsequent operations were essentially as described by Haworth and Percival (*loc. cit.*) and yielded finally a mobile syrup (6 g.), which was fractionally distilled at 0·03 mm.: (1) 2·2 g., b. p. 105—125° (all the b. p.'s in this paper are bath temperatures), $n_D^{14°}$ 1·4506; (2) 1·6 g., b. p. 125—140°, $n_D^{14°}$ 1·4498, OMe 58%; (3) 0·2 g., b. p. 145—170°, $n_D^{14°}$ 1·4556; (4) 1·1 g., b. p. 180—220°, $n_D^{14°}$ 1·4734, $[\alpha]_D^{14°}$ −4° (Found: C, 52·5; H, 8·0; OMe, 47·5; CO_2Me, 12·5%).

Pentamethyl methyl d-*galactonate.* After standing in the refrigerator, fraction (2) partially crystallised; the crystals were separated on a porous tile and recrystallised from light petroleum (b. p. 60—80°), yielding 0·9 g., m. p. 46°, $[\alpha]_D^{14°}$ +20° in water (*c*, 0·4) (Found: C, 51·6; H, 8·7; OMe, 64·3; CO_2Me, 19·6. $C_{12}H_{24}O_7$ requires C, 51·4; H, 8·6; OMe, 66·4; CO_2Me, 21·0%).

2 : 5-*Dimethyl* 3 : 6-*anhydro*-l-*galactonic acid.* Fraction (4) (0·63 g.) was heated at 95—100° with 5% sulphuric acid (20 c.c.); $[\alpha]_D^{14°}$ −8° (initial); +16° (160 mins., constant value). Neutralisation with barium carbonate and extraction with ether gave a mobile syrup (0·3 g.), which yielded on treatment with aniline tetramethyl *d*-galactopyranose anilide (0·2 g.), m. p. and mixed m. p. 196°. The residue of barium salts was treated with sulphuric acid, and a syrup was obtained which crystallised on the addition of chloroform to yield an acid (0·08 g.), m. p. 160°, $[\alpha]_D^{18°}$ −65° in water (*c*, 0·5)(Found: C, 46·2; H, 7·0; OMe, 28·0; equiv. by titration, 206. $C_8H_{14}O_6$ requires C, 46·6; H, 6·8; OMe, 30·0%; equiv., 212).

2 : 4-Dimethyl 3 : 6-anhydro-*l*-galactonic acid, prepared from the corresponding β-methylgalactoside by Haworth and Smith's method (*loc. cit.*), had m. p. 151°, mixed m. p. with the above 125—130°. A small portion of the acid on treatment with diazomethane and then with methyl-alcoholic ammonia yielded a crystalline amide, which gave a negative Weerman reaction and after recrystallisation from acetone had m. p. 171°.

Further Experiments on the Disaccharide Acids.—The syrupy product accompanying the above crystalline acid was not investigated further on this occasion, but, in other experiments, probably owing to the difficulty of controlling the conditions of acetolysis, the main product was a syrup.

A fraction (1·9 g.), b. p. 180—210°/0·08 mm., $n_D^{14°}$ 1·4755, $[\alpha]_D^{14°}$ −7° (OMe, 54·2%), corresponding to fraction (4) above, obtained from 32 g. of methylated agar, after a further methylation with methyl iodide and silver oxide (1·4 g.), was hydrolysed for 3 hours with 5% sulphuric acid. Neutralisation with barium carbonate and treatment as before gave tetramethyl *d*-galactopyranose anilide (0·5 g.), m. p. and mixed m. p. 197°, $[\alpha]_D^{18°}$ −78° in acetone (*c*, 1·0) (Found: OMe, 38·5. Calc. for $C_{16}H_{25}O_5N$: OMe, 39·9%). Treatment of the insoluble residue with sulphuric acid gave a syrup 0·65 g.), $[\alpha]_D^{14°}$ −3° in water (*c*, 1·5) (Found: OMe, 46·1; equiv. by titration, 245. $C_{10}H_{20}O_7$ requires OMe, 49·2%; equiv., 251). This acid was heated at 100°/15 mm. for 10 hours, but no change in properties was observed.

Esterification of the acid (0·5 g.) with diazomethane, followed by distillation at 110—135°/0·07 mm., gave an ester

(0·4 g.), $n_D^{18°}$ 1·4503, $[\alpha]_D^{15°}$ +11° in water (*c*, 1·0) (Found: OMe, 56·2; CO_2Me, 20·1. $C_{11}H_{22}O_7$ requires OMe, 58·3; CO_2Me, 22·2%). A portion (0·1 g.), treated with methyl-alcoholic ammonia, gave a syrupy amide which gave a negative Weerman test. The remaining ester on methylation with methyl iodide and silver oxide, followed by distillation at 110°/0·50 mm., gave crystalline pentamethyl methyl galactonate, m. p. 46°, not depressed by an authentic specimen, $[\alpha]_D^{16°}$ +19° in water (*c*, 1·1).

The Hydrolysis of Methylated Agar and End Group Investigation.—Methylated agar (32 g.) (OMe, 32·9%) was hydrolysed with methyl-alcoholic hydrogen chloride (1 l.) at 75° for 40 hours. Neutralisation with silver carbonate, filtration, and removal of solvent gave a syrup (33·4 g.), which was distilled at 0·03 mm. to yield the following fractions: (1) 15·6 g., b. p. 125—145°, crystalline; (2) 1·4 g., b. p. 145—150°; (3) 2·4 g., b. p. 165—175°; (4) 14·0 g., residue. Fraction (1) was recrystallised from light petroleum (b. p. 60—80°) (500 c.c.) so that about 80% of the trimethyl methyl-galactoside content was deposited rapidly, and the filtrate was evaporated to yield a semi-solid mass (3·1 g.), which was then distilled from a flask with a vacuum-jacketed spiral column to yield three crystalline fractions: (*a*) 0·67 g., b. p. 120—130°, $[\alpha]_D^{14°}$ +100° in water (c, 1·0), OMe 51·1%; (*b*) 1·3 g., b. p. 130—140°, OMe 50·9%; (*c*) 0·24 g., b. p. 140—160°.

Fraction (*a*), kept for 24 hours at room temperature with 0·8N-sulphuric acid, suffered no change in rotation, proving the absence of 2 : 4-dimethyl 3 : 6-anhydro-β-methyl-*l*-galactoside. Subsequent hydrolysis of the glycosides at 95—100°, followed by anilide formation in the usual way, gave none of the easily crystallisable tetramethyl galactopyranose anilide, but 2 : 4 : 6-trimethyl *d*-galactose anilide, m. p. 178°, was obtained.

Fraction (3) was extracted with light petroleum (b. p. 60—80°), and gave a residual syrup (2·0 g.) which after two methylations with methyl iodide and silver oxide gave 2 : 4-dimethyl 3 : 6-anhydro-β-methyl-*l*-galactoside (0·4 g.). The light petroleum extracts were evaporated and the syrup (0·3 g.) obtained was methylated three times with methyl iodide and silver oxide. Hydrolysis and anilide formation gave an anilide (0·03 g.), m. p. 197°, $[\alpha]_D^{20°}$ +70° in acetone (*c*, 0·8), mixed m. p. with tetramethyl *d*-galactopyranose anilide, 185°. This must therefore be characterised as *tetramethyl* l-*galactose anilide* (Found: C, 61·1; H, 7·9; OMe, 37·6; N, 4·6. $C_{16}H_{25}O_5N$ requires C, 61·7; H, 8·1; OMe, 39·9; N, 4·5%).

Fraction (4) was hydrolysed as above for a further 24 hours and the glycosides on distillation at 0·05 mm. gave the following fractions: (5) 2·5 g., b. p. 115—125°, crystalline; (6) 4·0 g., b. p. 125—145°, crystalline; (7) 3·9 g., b. p. 150—175°; (8) 2·9 g., b. p. 175—200°; (9) 1·5 g., residue.

Fractions (5) and (6) were combined and recrystallised from light petroleum to give 2 : 4 : 6-trimethyl methylgalactosides (5·5 g.), m. p. 60°. The residual syrup on hydrolysis and anilide formation gave no tetramethyl galactopyranose anilide. Fractions (7) and (8) were combined and distilled from a smaller flask to give (10) 1·7 g., b. p. 135—150°, $n_D^{16°}$ 1·4712, partly crystalline; (11) 2·8 g., b. p. 155—175°, $n_D^{16°}$ 1·4706, $[\alpha]_D^{16°}$ +4° in water, OMe 40·2%; (12) 1·0 g., b. p. 175—200°, $n_D^{16°}$ 1·4688, $[\alpha]_D^{16°}$ +3° in water, OMe 38·7%; (13) 1·4 g., residue.

Fraction (11) was extracted repeatedly with boiling light petroleum (b. p. 60—80°) and the residue was combined with fraction (12) and heated at 95—100° with 5% sulphuric acid for 24 hours to decompose anhydro-sugars. After neutralisation with barium carbonate, filtration, and evaporation the residual syrup (3·4 g.; OMe 26%) was submitted to glycoside formation with 5% methyl-alcoholic hydrogen chloride at 70° for 8 hours; the product, obtained in the usual way, distilled at 0·03 mm. as a syrup (2·9 g.), b. p. 170—185°, $n_D^{16°}$ 1·4700 (Found: OMe, 41·0. Calc. for $C_9H_{18}O_6$:OMe, 41·9%).

Complete methylation and isolation of tetramethyl galactopyranose anilide. The syrup (0·5 g.) was methylated four times with silver oxide and methyl iodide, and the product converted into the anilide. Tetramethyl *d*-galactopyranose anilide (0·3 g.), m. p. 197°, not depressed by an authentic specimen, $[\alpha]_D^{17°}$ −72° in acetone (*c*, 1·0), was obtained.

Osazone formation. The syrup (1·0 g.; OMe, 41·0%) was hydrolysed with 8% hydrochloric acid at 95—100° for 2½ hours. The sugar isolated had $[\alpha]_D^{16°}$ +30° in water (*c*, 1·5) (Found: OMe, 26·4. Calc. for $C_6H_{14}O_6$:OMe, 29·8%).

Treatment with phenylhydrazine acetate gave a tarry osazone, which could be precipitated from chloroform solution by light petroleum as a brown powder (Found: OMe, 7·5. Calc. for $C_{18}H_{24}O_4N_4$: OMe, 8·3%).

The Hydrolysis of Agar at 130°.—Washed agar (100 g.) was heated in an autoclave at 130° with water (2 l.) for 5 hours. The gel was separated in a centrifuge and purified by solution thrice in hot water, cooling, and centrifuging; dehydration with alcohol followed and the powdered product "δ" (40 g.) was dried in a vacuum over calcium chloride. The clear brown solution accompanying this material had p_H 4·7, determined by the quinhydrone electrode. It was concentrated at 48°/15 mm. to 500 c.c. and poured into alcohol (2 l.). The precipitated product "λ" was purified thrice by solution in water and precipitation with alcohol, dehydrated, and dried as before (17 g.).

Experiments on Hydrato-kanten "δ."—This substance was a greyish-white powder (ash, 0·5%), slightly reducing to Fehling's solution, and 0·03 g. in 5 c.c. of water formed a gel. The iodine number determined according to Bergmann and Machemer (*Ber.*, 1930, **63**, 316) was 2·47, corresponding to a unit of 8100 per reducing group. The iodine number for washed agar was 1·25, corresponding to a value of 16,000.

Acetylation and fractionation of the "δ" acetate. Powdered "δ" (45 g.) was acetylated with pyridine and acetic anhydride. Fractional precipitation (48 g.) from chloroform by light petroleum yielded three fractions (Table III). When deacetylated, each of these fractions formed a gel with water (0·05 g. in 3 c.c.). The apparent molecular weight (M_v) was calculated from $\eta_{sp.} = c.M_v.10^{-3}$, the repeating unit being reckoned as $[C_6H_7O_2(OAc)_3]$.

TABLE III.

	% CH_3·CO.	$[\alpha]_D^{14°}$.	$\eta_{sp.}^{20°}$.	*c*.	M_v.
Agar acetate	36·4	−32·1°	0·343	0·336	29,400
(1) (6 g.)	34·1	−33·3	0·125	0·427	8,400
2) (24 g.)	36·0	−32·5	0·158	0·428	10,600
(3) (9 g.)	36·5	−31·8	0·131	0·415	9,100

Deacetylation and methylation. Fraction (2), dissolved in acetone, was deacetylated and methylated, the product being remethylated twice, purified, and fractionated (17 g.) (Table IV).

TABLE IV.

	% OMe.	$[\alpha]_D^{14°}$.	$\eta_{sp.}^{20°}$.	*c*.	M_v.
Methylated agar	32·1	−86°	0·266	0·349	15,500
(1) (3·1 g.)	32·0	−79	0·172	0·418	8,400
(2) (7·0 g.)	32·5	−80	0·168	0·441	7,800
(3) (6·9 g.)	32·1	−86	0·152	0·418	7,400

Hydrolysis of methylated " δ." Methylated " δ " (9·5 g.) was hydrolysed with methyl-alcoholic hydrogen chloride, and the products, divided into 10 fractions by distillation in a high vacuum, treated as described in Part II (*loc. cit.*) to yield trimethyl methylgalactosides (4·96 g., 52%) and 2 : 4-dimethyl 3 : 6-anhydro-β-methyl-*l*-galactoside (1·05 g., 11%). On the assumption that the completely methylated syrups (2·3 g.) from which the 2 : 4-dimethyl β-methyl-*l*-galactoside crystallised contained 16% of this material (see Part II, *loc. cit.*) the proportion of the latter substance becomes 14·9%.

Hydrato-kanten " λ."—This substance was a white powder (ash, 2·5%), soluble in cold water and reducing to Fehling's solution. The iodine number was 5·89, corresponding to a unit of 3,400 per reducing group.

Acetylation was carried out as above and the acetate (14 g.), obtained in good yield, was divided into three fractions by precipitation by light petroleum from chloroform solution (Table V). Methylation, carried out as described above, gave a product (4·5 g.), which was fractionally precipitated (Table VI).

TABLE V.

	% CH_3·CO.	$[\alpha]_D^{14°}$.	$\eta_{sp.}^{20°}$.	*c*.	M_v.
1	38·7	−45°	0·077	0·410	5,400
2	40·7	−37	0·053	0·368	4,100
3	41	−36	0·062	0·437	4,100

TABLE VI.

	% OMe.	$[\alpha]_D^{14°}$.	$\eta_{sp.}^{20°}$.	*c*.	M_v.
1	32·5	−100°	0·115	0·452	5,200
2	34·5	− 80	0·092	0·446	4,200
3	35·0	− 78	0·081	0·401	4,100

Hydrolysis of methylated " λ." Methylated " λ " (11·2 g.) was hydrolysed, and the products (8 fractions) investigated as for " δ " to yield trimethyl methylgalactosides (6·21 g., 59·1%) and 2 : 4-dimethyl 3 : 6-anhydro-β-methyl-*l*-galactoside (0·95 g., 9·1%). On the assumption that the syrups from which the latter substance crystallised contained 16% of this material, the proportion becomes 13·3%.

Autohydrolysis of " δ."—The finely powdered substance (20 g.) was heated with water (200 c.c.) for 2½ hours at 130°. The resultant thin gel was centrifuged, and the product purified as described previously. The greyish-white powder (8 g.) was reducing to Fehling's solution and the iodine number of 6·1 corresponds to a unit of 3,300 per reducing group. This substance " δ_1 " formed a gel with water (0·08 g. in 2 c.c.).

Acetylation as described above, followed by fractionation (3·8 g.), gave : fraction (1) 1·5 g., $[\alpha]_D^{14°}$ −35°, $\eta_{sp.}^{20°}$ 0·090 in *m*-cresol, (*c*, 0·441), M_v 5,900, CH_3·CO 37·8%; fraction (2) 2·1 g., $[\alpha]_D^{14°}$ −30°, $\eta_{sp.}^{20°}$ 0·087 in *m*-cresol (*c*, 0·412), M_v 6,100, CH_3·CO 38·0%.

Powdered " δ " (20 g.) was heated for 4½ hours at 130° with water (400 c.c.). No solid remained and no substance was obtained on precipitation with alcohol. " δ " is thus not transformed into " λ " in this way.

Autohydrolysis of " λ."—The powdered " λ " (10 g.) was heated with water (200 c.c.) for 1½ hours at 130°. The product on precipitation with alcohol appeared unchanged and gave the same iodine number (5·87) as the starting material. Further autohydrolysis (3½ hours) gave a product " λ_1 " (7·1 g.) with an iodine number of 17·0, corresponding to a unit of 1,200 per reducing group.

Acetylation was followed by fractionation (3·4 g.) : fraction (1) 0·8 g., $[\alpha]_D^{14°}$ −43°, $\eta_{sp.}^{20°}$ 0·073 in *m*-cresol (*c*, 0·417), M_v 5,000, CH_3·CO 40·0%; fraction (2) 2·5 g., $[\alpha]_D^{14°}$ −37°, $\eta_{sp.}^{20°}$ 0·037 in *m*-cresol (*c*, 0·433), M_v 2,500, CH_3·CO 44·1%.

Methylated agar was recovered unchanged on heating with water for 3½ hours at 130°.

Thanks are expressed to the Earl of Moray Endowment and Imperial Chemical Industries Ltd. for grants and to the Carnegie Trust for the award of a Teaching Fellowship to one of us (E. G. V. P.).

KING'S BUILDINGS, UNIVERSITY OF EDINBURGH. [*Received, August 31st,* 1942.]

---

167. p-*Aminodimethylaniline. Part II. The* o-*Chloro- and -Nitro-derivatives.*

By ERNEST E. AYLING, JOHN H. GORVIN, and LEONARD E. HINKEL.

Methods are described for the preparation of 2-chloro-, 2 : 6-dichloro-, and 2-chloro-6-nitro-4-aminodimethylaniline. A novel reaction is recorded in which bromine removes an *N*-methyl group, leading to the formation of 2-chloro-6-nitro- and 2 : 6-dinitro-4-acetamidomethylaniline.

IN Part I (J., 1941, 613) the authors showed that the sluggishness of the reaction between diazotised *p*-aminodimethylaniline and amines or phenols, and the poor yields of azo-compound, can be attributed to the strong tautomeric influence of the dimethylamino-group, which hinders the formation of a positive charge at the diazo-group. In order to study the possible modification of this effect by nuclear substituents, such as chlorine and the nitro-group, in the *o*-position to the dimethylamino-group, it was necessary to examine the mode of formation and the properties of such compounds, only 2 : 6-dinitro-4-aminodimethylaniline (Hodgson and Crook, J., 1934, 873) having previously been described.

Although 2-nitro-4-aminodimethylaniline is known as its acetyl and formyl derivatives (*idem*, J., 1932, 2976; Pinnow and Pistor, *Ber.*, 1894, **27**, 605), the free base has not been isolated, since it suffers decomposition during its liberation by hydrolysis. An attempt to obtain the base by partial reduction of 2 : 4-dinitrodimethylaniline yielded only 4-nitro-2-aminodimethylaniline (compare Heim, *Ber.*, 1888, **21**, 2308), and the nitration of *p*-aminodimethylaniline gave the 2 : 6-dinitro-base.

2-*Chloro*-4-*aminodimethylaniline* was obtained by hydrolysis of its *acetyl* derivative, formed in the chlorination

of *p*-acetamidodimethylaniline in chloroform. It was also readily obtained not only from 2-nitro-4-acetamidodimethylaniline, by reduction of the nitro-group and replacement of the resulting amino-group by chlorine by means of the diazo-reaction and subsequent hydrolysis, but also by reduction of 2-chloro-4-nitrodimethylaniline (compare van Duin, *Rec. Trav. chim.*, 1932, **51**, 878). The latter compound results from direct chlorination of 4-nitrodimethylaniline or from the diazo-reaction on 4-nitro-2-aminodimethylaniline, which, when diazotised, resembles diazotised *p*-aminodimethylaniline (Ayling, Gorvin, and Hinkel, *loc. cit.*) in its anomalous reaction with copper bronze but reacts normally with cuprous chloride.

When nitrated in acetic acid solution, the 2-nitro- or 2-chloro-4-acetamidodimethylaniline acquires a nitro-group in the 6-position and a nitroso-group replaces an *N*-methyl group (compare Meldola and Hollely, J., 1915, **107**, 610). In hydrochloric acid (*d*, 1·2), however, the reaction can be arrested at the first stage to give 2 : 6-dinitro- and 2-*chloro*-6-*nitro*-4-*acetamidodimethylaniline*, respectively. The latter compound also resulted from direct chlorination of 2-nitro-4-acetamidodimethylaniline. The acetyl group could not be removed by hydrolysis without decomposition of the base (compare 2-nitro-4-acetamidodimethylaniline). Replacement of the nitro-group in 2-nitro-6-chloro-4-acetamidodimethylaniline by chlorine, through the amine by means of the diazo-reaction in the usual manner, yielded 2 : 6-*dichloro*-4-*acetamidodimethylaniline*. This compound also results from the direct chlorination of 2-chloro-4-acetamidodimethylaniline.

A new example of the weakening of the bond between the *N*-methyl groups and the nitrogen atom by *o*-substituents (compare Hodgson, *J. Soc. Dyers Col.*, 1930, **46**, 183; Emerson, *J. Amer. Chem. Soc.*, 1941, **63**, 2023) is provided by the action of bromine on 2-chloro-6-nitro-4-acetamidodimethylaniline and on 2 : 6-dinitro-4-acetamidodimethylaniline. In each case there is an elimination of an *N*-methyl group to give the corresponding monomethylaniline derivative (compare Leymann, *Ber.*, 1882, **15**, 1234).

Experimental.

2-Nitro-4-acetamidodimethylaniline, prepared in 90% yield from *p*-acetamidodimethylaniline (Auwers and Wehr, *Annalen*, 1904, **344**, 311) by Pinnow and Pistor's method (*loc. cit.*) for the formyl analogue, crystallised from hot water, or appropriately seeded benzene solutions, in maroon parallelepipeds, m. p. 132° (cf. Hodgson and Crook, *loc. cit.*), or from benzene in orange-yellow needles, m. p. 122—123° (Found : N, 18·3. Calc. : N, 18·8%). The orange form also separated as a crystalline powder on neutralising cold, dilute aqueous acid solutions; van Alphen (*Rec. Trav. chim.*, 1932, **51**, 458) quotes many examples of dimorphism in nitro-compounds of similar type. The compound reacted readily with hot mineral acids but formed red tarry products.

When the filtrate from the above preparation was made alkaline with ammonia and evaporated to small bulk under reduced pressure, N-*nitroso*-4-*acetamidomethylaniline* (0·88 g., 6%) separated; after decolorisation, it crystallised from water in colourless plates, m. p. 146° (Found : C, 55·9; H, 5·7; N, 21·5. $C_9H_{11}O_2N_3$ requires C, 55·9; H, 5·7; N, 21·8%). The compound gives a positive reaction in the Liebermann nitrosoamine test (Hodgson and Crook, *loc. cit.*, obtained an *N*-nitroso-compound, m. p. 146°, when the above nitration was carried out in dilute hydrochloric acid).

Nitration of p-*Aminodimethylaniline.*—Nitric acid (*d* 1·5; 1·9 c.c., 2 mols.) in acetic acid (5 c.c.) was added to an ice-cooled solution of *p*-aminodimethylaniline (2·7 g., 1 mol.) in acetic acid (20 c.c.) containing sulphuric acid (1·2 c.c., 1 mol.). Reaction was rapid, and when the product was poured into water (250 c.c.) 2 : 6-dinitro-4-aminodimethylaniline (0·24 g.) separated; after decolorisation, this crystallised from aqueous alcohol in orange-red needles, m. p. 157°, unchanged by admixture with an authentic specimen prepared by the method of Hodgson and Crook (*loc. cit.*).

2 : 4-*Dinitrodimethylaniline.*—Following a method mentioned, but not detailed, by Orton (*Ber.*, 1907, **40**, 374), nitric acid was added to a solution of dimethylaniline (60 g.) in acetic acid (225 c.c.). On addition of a little sodium nitrite a rapid reaction set in, during which the mixture was kept below 15° by cooling in ice. When crystals appeared in the solution, the temperature was no longer controlled and, at the end of the reaction, 2 : 4-dinitrodimethylaniline (78 g., 77%) was obtained by filtration below 0°. On dilution with water, more of the compound was obtained. Crystallisation from alcohol gave golden prisms, m. p. 87°.

4-*Nitro*-2-*aminodimethylaniline.*—A solution of crystalline stannous chloride (67·8 g.) in alcoholic hydrogen chloride (100 c.c.) was added to a warm solution of 2 : 4-dinitrodimethylaniline (21·1 g.) in alcohol (100 c.c.). The mixture was cooled, diluted to 800 c.c., and 50% sodium hydroxide solution added until all the precipitated stannic hydroxide had redissolved. The red crystals which separated overnight were dissolved in warm hydrochloric acid (20 c.c.) and the solution was diluted. A small amount of unchanged 2 : 4-dinitrodimethylaniline separated and was removed. Addition of alkali to the filtrate liberated 4-nitro-2-aminodimethylaniline (13 g., 72%), which crystallised from water in orange-yellow needles, m. p. 63° (cf. Heim, *loc. cit.*). The base (2 g.) and acetic anhydride (2 g.) were boiled for 3 mins.; cooling and basification then yielded 4-*nitro*-2-*acetamidodimethylaniline*, which crystallised from alcohol in long, straw-coloured needles, m. p. 163° (Found : N, 19·0. $C_{10}H_{13}O_3N_3$ requires N, 18·8%).

Benzaldehyde (1·5 g.) was added to a boiling solution of 4-nitro-2-aminodimethylaniline (2 g.) in alcohol (20 c.c.). On cooling, the *benzylidene* derivative separated; it crystallised from alcohol in golden needles, m. p. 128° (Found : N, 15·2. $C_{15}H_{15}O_2N_3$ requires N, 15·6%).

2-*Chloro*-4-*acetamidodimethylaniline.*—(a) *From* p-*acetamidodimethylaniline.* Chlorine was passed into a solution of the base (20 g.) in dry chloroform (300 c.c.) at room temperature. The mixture developed an intensely crimson colour, due probably to the formation of a Wurster salt (cf. Sidgwick, "The Organic Chemistry of Nitrogen," 1937, 99); this colour gradually disappeared with the separation of a colourless, crystalline hydrochloride. This was washed with chloroform, dissolved in warm water, and the solution made alkaline, whereupon 2-*chloro*-4-*acetamidodimethylaniline* (13·8 g., 58%) separated; several crystallisations from alcohol yielded colourless prisms, m. p. 119—120° (Found : N, 13·0. $C_{10}H_{13}ON_2Cl$ requires N, 13·2%).

(b) *From* 2-*nitro*-4-*acetamidodimethylaniline.* The nitro-compound (3 g.) in alcohol (15 c.c.) was reduced with a warm saturated aqueous solution of sodium hyposulphite (dithionite). After cooling to 0°, hydrochloric acid was added, and the solution diazotised with sodium nitrite. Cuprous chloride in hydrochloric acid (10% solution) was added, and the solution warmed; cooling and addition of excess of ammonia then gave a small amount of 2-chloro-4-acetamidodimethylaniline (mixed m. p.).

2-*Chloro*-4-*aminodimethylaniline.*—The foregoing compound was hydrolysed by 3 mins.' boiling with concentrated hydrochloric acid. On cooling and basifying, 2-*chloro*-4-*aminodimethylaniline* separated as a colourless solid, which crystallised from light petroleum (b. p. 60—80°) in prisms or leaflets, m. p. 61·5—63° (Found : Cl, 20·9. $C_8H_{11}N_2Cl$

requires Cl, 20·8%). The base, which is somewhat soluble in water, does not give Lauth's test for *p*-diamines; it does not darken in air.

Action of Copper-bronze on Diazotised 4-*Nitro*-2-*aminodimethylaniline.*—The base (1 g.) in hydrochloric acid (5 c.c.) was diazotised with sodium nitrite (0·38 g.) in water. Copper-bronze (0·5 g.) was added, and the solution filtered and made alkaline with ammonia; *p*-nitrodimethylaniline separated, and crystallised from alcohol in needles, m. p. 163°, unchanged by an authentic specimen. The same compound was obtained when the above diazo-solution was refluxed with methyl alcohol and when solutions of the diazotised base in nitric acid were treated with copper-bronze or with freshly prepared cuprous oxide.

2-*Chloro*-4-*nitrodimethylaniline.*—(a) *From* p-*nitrodimethylaniline.* Chlorine was led into a solution of the nitro-compound (8·3 g., 1 mol.) (Weber, *Ber.*, 1877, **10**, 761) in chloroform (200 c.c.) at room temperature until the increase in weight was 3·6 g. (1 mol. of chlorine). The solution was then extracted with concentrated hydrochloric acid and the acid extract, after being boiled to remove chloroform, was cooled and basified. 2-Chloro-4-nitrodimethylaniline (7·5 g., 75%) separated; it crystallised from alcohol in golden plates, m. p. 78° (cf. van Duin, *loc. cit.*) (Found: Cl, 17·5. Calc., Cl, 17·7%).

(b) *From* 4-*nitro*-2-*aminodimethylaniline.* The base (30 g.), dissolved in hydrochloric acid (50 c.c.) and water (50 c.c.), was diazotised at 10° with sodium nitrite (11·5 g.), and the solution slowly poured into 100 c.c. of a 10% solution of cuprous chloride in boiling hydrochloric acid. After the mixture had cooled, excess of ammonia was added, and the resulting precipitate removed, dried, and extracted (Soxhlet) with alcohol. The extract yielded 2-chloro-4-nitrodimethylaniline (24 g., 70%).

Reduction of 2-*Chloro*-4-*nitrodimethylaniline.*—A solution of the base (36 g.) and crystalline stannous chloride (170 g.) in hydrochloric acid (300 c.c.) was heated to boiling. On cooling, 2-*chloro*-4-*aminodimethylaniline stannichloride* (77 g., 86%) separated in silvery needles, purified by boiling with alcohol (Found: Sn, 23·4. $C_9H_{11}N_2Cl,H_2SnCl_6$ requires Sn, 23·6%). The amine separated when a solution of the stannichloride in water was decomposed with excess of 50% sodium hydroxide solution.

Nitration of 2-*Nitro*-4-*acetamidodimethylaniline.*—(i) *In acetic acid.* Nitric acid (*d* 1·42, 4 c.c.) was added to a solution of the acetyl compound (2 g.) in acetic acid (16 c.c.) at 15°. After an hour the solution was diluted with water (200 c.c.); 2 : 6-dinitro-*N*-nitroso-4-acetamidomethylaniline (2 g.) separated, and crystallised from alcohol in colourless needles, m. p. 152°, unchanged by an authentic specimen prepared according to Meldola and Hollely (*loc. cit.*).

(ii) *In hydrochloric acid.* Hydrochloric acid (10 c.c.) was used as solvent, the other conditions being as in (i). After several minutes the clear golden solution was diluted and made alkaline, whereupon 2 : 6-dinitro-4-acetamidodimethylaniline (1·6 g.) separated; it crystallised from alcohol in orange prisms, m. p. 195°, unchanged by a specimen prepared according to Hodgson and Crook (*loc. cit.*).

Nitration of 2-*Chloro*-4-*acetamidodimethylaniline.*—(i) *In acetic acid.* The procedure was exactly analogous to that in (i) above. 2-*Chloro*-6-*nitro*-N-*nitroso*-4-*acetamidomethylaniline* (1·8 g.) separated; it was crystallised several times from chloroform–carbon tetrachloride and finally from aqueous alcohol, forming colourless needles, m. p. 132—133° (Found: N, 20·0; Cl, 13·2. $C_9H_9O_4N_4Cl$ requires N, 20·6; Cl, 13·0%); it gave a positive reaction in the Leibermann nitrosoamine test.

(ii) *In hydrochloric acid.* Nitric acid (*d* 1·42; 15 c.c.) was added to a solution of the base (5 g.) in hydrochloric acid (30 c.c.) at room temperature. After several minutes the clear golden solution was diluted and basified; 2-*chloro*-6-*nitro*-4-*acetamidodimethylaniline* (5·2 g., 86%) separated, and crystallised from aqueous acetic acid or aqueous alcohol in orange-yellow prisms or needles, m. p. 165—166° (Found: Cl, 13·85. $C_{10}H_{12}O_3N_3Cl$ requires Cl, 13·8%).

Oxidation of 2-*Chloro*-6-*nitro*-N-*nitroso*-4-*acetamidomethylaniline.*—The nitrosoamine (2 g.) was dissolved in nitric acid (15 c.c., *d*, 1·5) at 0°, and the solution kept for an hour at room temperature. Dilution with water yielded 2-*chloro*-6:*N*-*dinitro*-4-*acetamidomethylaniline*, which crystallised from ethyl acetate–light petroleum (b. p. 80—100°) and then from aqueous alcohol in colourless needles, m. p. 152—153° (Found: Cl, 12·1. $C_9H_9O_5N_4Cl$ requires Cl, 12·3%). When this compound is dissolved in acetic acid containing α-naphthylamine and warmed with zinc dust, a red colour develops (Franchimont–Bamberger test for *N*-nitro-compounds).

Chlorination of 2-*Nitro*-4-*acetamidodimethylaniline.*—Chlorine was led into a solution of the base (18 g.) in dry chloroform (300 c.c.) at room temperature. The white solid which separated was washed with chloroform and treated with water at 100°. The 2-chloro-6-nitro-4-acetamidodimethylaniline (2·2 g.) obtained on cooling the solution, crystallised from aqueous alcohol in orange-yellow needles, m. p. 165—166°, unchanged by admixture with the compound obtained by nitration of 2-chloro-4-acetamidodimethylaniline. When the aqueous filtrate from the reaction was basified, much unchanged 2-nitro-4-acetamidodimethylaniline was recovered.

Chlorination of 2-*Chloro*-4-*acetamidodimethylaniline.*—Chlorine was led into a solution of the base (10 g.) in chloroform (160 c.c.) at room temperature, the white solid (10·5 g.) being treated as in the preceding case. The 2 : 6-*dichloro*-4-*acetamidodimethylaniline* (1·74 g.), obtained when the solution was cooled and filtered, crystallised from aqueous alcohol in colourless plates, m. p. 153—154° (Found: Cl, 29·0. $C_{10}H_{12}ON_2Cl_2$ requires Cl, 28·7%). Again, much unchanged starting material was recovered.

A similar reaction to the above occurred when the requisite amount of " dichloramine " was added to 2-chloro-4-acetamidodimethylaniline in chloroform solution.

2-*Chloro*-6-*amino*-4-*acetamidodimethylaniline.*—2-Chloro-6-nitro-4-acetamidodimethylaniline (5 g.) in alcohol (75 c.c.) was reduced with a saturated aqueous solution of sodium hyposulphite (dithionite). Basification and concentration of the solution yielded the 6-*amino*-compound, which crystallised from aqueous alcohol in colourless plates, m. p. 152° (Found: Cl, 15·5. $C_{10}H_{14}ON_3Cl$ requires Cl, 15·6%).

2 : 6-*Dichloro*-4-*acetamidodimethylaniline.*—2-Chloro-6-amino-4-acetamidodimethylaniline (1·5 g.) in hydrochloric acid (10 c.c.) and water (5 c.c.) was diazotised at 10° with sodium nitrite (0·45 g.) in water (5 c.c.), and copper-bronze (0·5 g.) added. Filtration and addition of ammonia yielded 2 : 6-dichloro-4-acetamidodimethylaniline (1·3 g., 80%) (m. p. and mixed m. p.).

2 : 6-*Dichloro*-4-*aminodimethylaniline.*—The foregoing compound was hydrolysed by 3 mins.' boiling with concentrated hydrochloric acid. Cooling and basification then yielded 2 : 6-*dichloro*-4-*aminodimethylaniline* as a colourless solid, which crystallised from light petroleum (b. p. 80—100°) or from aqueous alcohol in needles, m. p. 90—91° (Found: Cl, 34·8. $C_9H_{10}N_2Cl_2$ requires Cl, 34·6%).

2-*Chloro*-6-*nitro*-4-*acetamidomethylaniline.*—2-Chloro-6-nitro-*N*-nitroso-4-acetamidomethylaniline was boiled with excess of phenol for 15 minutes. Cooling and basification yielded 2-*chloro*-6-*nitro*-4-*acetamidomethylaniline*, which separated from alcohol as a bright red, crystalline powder, m. p. 208—209° (Found: Cl, 14·6. $C_9H_{10}O_3N_3Cl$ requires Cl, 14·55%). The same product was obtained when 2-chloro-6 : *N*-dinitro-4-acetamidomethylaniline was submitted to this procedure.

Action of Bromine on 2-*Chloro*-6-*nitro*-4-*acetamidodimethylaniline.*—Bromine (0·64 g.) in chloroform (20 c.c.) was added to a solution of the base (1·04 g.) in chloroform (10 c.c.). The oil which separated crystallised overnight to a yellow solid, which with boiling water yielded 2-chloro-6-nitro-4-acetamidomethylaniline (0·87 g., 94%) (m. p. and mixed m. p.).

Action of Bromine on 2 : 6-*Dinitro-4-acetamidodimethylaniline.*—The base (0·7 g.) was treated as above with bromine (0·42 g., 1 mol.) in chloroform. The resulting 2 : 6-dinitro-4-acetamidomethylaniline separated from alcohol as a red crystalline powder, m. p. 196—197°, unchanged by an authentic specimen prepared according to Meldola and Hollely (*loc. cit.*).

The authors' thanks are due to Imperial Chemical Industries, Ltd. (Dyestuffs Group), for a grant.

UNIVERSITY COLLEGE, SWANSEA. [*Received, July 29th,* 1942.]

NOTE.

Some Quinoline Derivatives of Sulphanilamide. By O. G. BACKEBERG and J. L. C. MARAIS.

2- and 4-SUBSTITUTED quinoline derivatives have been prepared by condensing sulphanilamide with the readily accessible 2-chlorolepidine and 4-chloroquinaldine and with the 6-methoxy- and the 6-ethoxy-derivative of the former and the 6- and 8-methoxy- and -ethoxy-derivatives of the latter. The compounds described are all substituted in the amino- or N^4-group; substitution in the sulphonamido- or N^1-group could not be effected with these chloro-compounds by Phillips' method (J., 1941, 9), or from the corresponding aminoquinolines (this vol., p. 381) and *p*-acetamidobenzenesulphonyl chloride. The nomenclature adopted is that suggested by Crossley, Northey, and Hultquist (*J. Amer. Chem. Soc.*, 1938, **60**, 2217).

3 G. (1 mol.) of the chloro-compound and sulphanilamide (1 mol.) were refluxed for 2—3 hours in glacial acetic acid solution (10—15 c.c.); in some cases the hydrochloride of the condensation product separated. After reaction, the whole was poured into 150 c.c. of water and neutralised with ammonia. The bases obtained (70—80% yield) were crystallised from dilute alcohol or dilute pyridine. The condensations were also carried out by heating the reactants at 180° for 15 minutes in the absence of a solvent (Bobranski, *Arch. Pharm.*, 1939, **277**, 75), but some of the quinaldine condensation products were contaminated with a coloured substance, and in these cases the fomer method of condensation was to be preferred.

N^4-(2′-*Lepidyl*)*sulphanilamide*, colourless plates, m. p. 258° (Found: C, 61·4; H, 4·8; N, 13·55. $C_{16}H_{15}O_2N_3S$ requires C, 61·35; H, 4·8; N, 13·4%).

N^4-(6′-*Methoxy*-2′-*lepidyl*)*sulphanilamide*, small, pale yellow plates, m. p. 249° (Found: C, 59·4; H, 5·2; N, 12·25. $C_{17}H_{17}O_3N_3S$ requires C, 59·5; H, 4·95; N, 12·25%).

N^4-(6′-*Ethoxy*-2′-*lepidyl*)*sulphanilamide*, small, pale yellow plates, m. p. 278° (Found: C, 60·7; H, 5·3; N, 11·8. $C_{18}H_{19}O_3N_3S$ requires C, 60·5; H, 5·3; N, 11·75%).

N^4-(4′-*Quinaldyl*)*sulphanilamide*, small, colourless plates, m. p. 280° (decomp.) (Found: C, 61·2; H, 4·85; N, 13·4. $C_{16}H_{15}O_2N_3S$ requires C, 61·35; H, 4·8; N, 13·4%).

N^4-(6′-*Methoxy*-4′-*quinaldyl*)*sulphanilamide*, small, colourless needles, m. p. 301° (decomp.) (Found: C, 59·7; H, 5·1; N, 12·3. $C_{17}H_{17}O_3N_3S$ requires C, 59·5; H, 4·95; N, 12·25%).

N^4-(8′-*Methoxy*-4′-*quinaldyl*)*sulphanilamide*, small, colourless needles, m. p. 293° (decomp.) (Found: C, 59·4; H, 5·05; N, 12·3%).

N^4-(6′-*Ethoxy*-4′-*quinaldyl*)*sulphanilamide*, small, colourless needles, m. p. 308° (decomp.) (Found: C, 60·35; H, 5·3; N, 11·9. $C_{18}H_{19}O_3N_3S$ requires C, 60·5; H, 5·3; N, 11·75%).

N^4-(8′-*Ethoxy*-4′-*quinaldyl*)*sulphanilamide*, small, colourless needles, m. p. 277° (decomp.) (Found: C, 60·3; H, 5·3; N, 11·9%).

The authors thank Professor H. Stephen for his interest in the work.—UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG, SOUTH AFRICA. [*Received, October 21st,* 1942.]

B. D. H. CHEMICALS

are of suitable purity for every scientific purpose

For work demanding the use of chemicals of the highest attainable standard of purity, use B.D.H. tested products. Accurate and consistent results can only be obtained by employing faultless reagents.

At this time it is appropriate to remind chemists that the B.D.H. manufacture the pure chemicals required in all kinds of research. Substances which hitherto were exclusively of foreign manufacture are now made by the B.D.H. to the very high standard of purity that distinguishes all B.D.H. products.

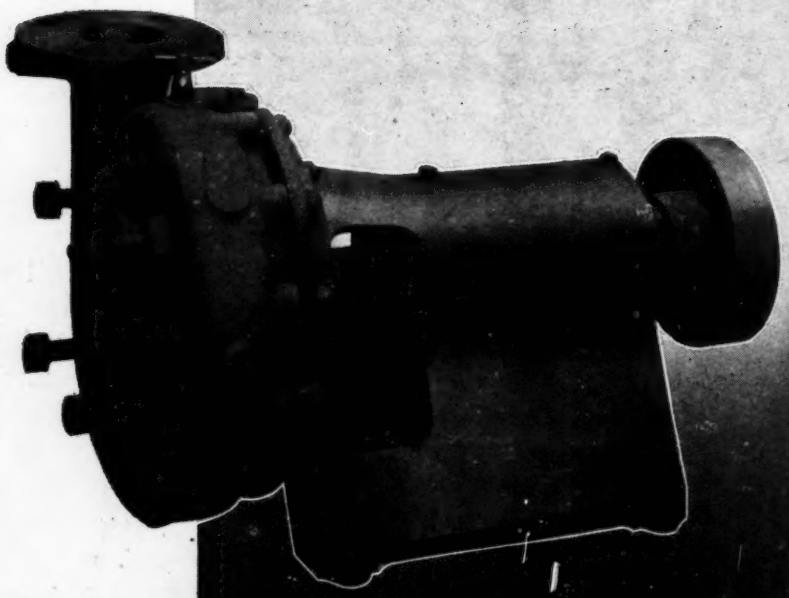
We invite inquiries for scientific chemicals for every purpose. A range of over 6000 separate articles of POSITIVE and GUARANTEED purity is shown in the B.D.H. Catalogue of Laboratory Chemicals which is sent on request to professional chemists.

Reagents in the 'AnalaR' series are guaranteed to conform to the specifications published in 'AnalaR' Standards for Laboratory Chemicals in which the stringent tests applied to 'AnalaR' chemicals are fully and explicitly defined.

THE BRITISH DRUG HOUSES LTD.

GRAHAM STREET LONDON, N.1

PUMPS *by the* **LEADING MAKERS**



CHV3 CHEMICAL PUMP manufactured by Pulsometer Engineering Co. Ltd. having casing and all working parts, including renewable sideplates of "Staybrite" FDP Steel. A "Staybrite" Steel blackplate is provided to prevent the liquor coming into contact with the cast iron hood. Duty is 250 g.p.m. against 50-ft. head at 1,440 r.p.m.

UTILISE TO THE FULL THE PROPERTIES OF

FIRTH-VICKERS "STAYBRITE"

REGD TRADE MARK

SUPER RUSTLESS STEEL

Owing to the large demand, we are at present greatly restricted as regards the purposes for which this steel can be supplied.

FIRTH-VICKERS STAINLESS STEELS LIMITED

Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk.

INDEX OF AUTHORS, 1942.

A.

Aarons, *E.*, and **Albert**, *A.*, 2-aminoacridine-7-sulphonamide, 183.
Abraham, *A. C.*, obituary notice of, 475.
Airs, *R. S.*, **Balfe**, *M. P.*, **Irwin**, *M.*, and **Kenyon**, *J.*, optical rotatory dispersion of (−)tetrahydrofurfuryl alcohol, 531.
Airs, *R. S.*, **Balfe**, *M. P.*, and **Kenyon**, *J.*, reactions of (+)- and (−)-γ-methyl-α-ethylallyl alcohols and their derivatives, 18.
Albert, *A.* See **Aarons**, *E.*
Allsebrook, *W. E.*, **Gulland**, *J. M.*, and **Story**, *L. F.*, constitution of purine nucleosides. Part X. Synthesis of xanthine and attempted syntheses of xanthine glucosides from glyoxalines, 232.
Ashley, *J. N.*, **Barber**, *H. J.*, **Ewins**, *A. J.*, **Newbery**, *G.*, and **Self**, *A. D. H.*, chemotherapeutic comparison of trypanocidal action of aromatic diamidines, 103.
Asker, (*Miss*) *W.* See **Schönberg**, *A.*
Astbury, *W. T.*, *X*-rays and stoicheiometry of proteins, with reference to structure of the keratin–myosin group, 337.
Audsley, *A.*, and **Goss**, *F. R.*, magnitude of the solvent effect in dipole-moment measurements. Part V. Solvent-effect constant and the moments of alkyl iodides, 358.
Audsley, *A.* See also **Goss**, *F. R.*
Ayling, *E. E.*, **Gorvin**, *J. H.*, and **Hinkel**, *L. E.*, *p*-aminodimethylaniline. Part II. *o*-Chloro- and -nitro-derivatives, 755.

B.

Backeberg, *O. G.*, and **Marais**, *J. L. C.*, reaction of 4-chloroquinaldines and of 2-chlorolepidines with ammonia, and preparation of the corresponding phenyl ethers, 381.
quinoline derivatives of sulphanilamide, 758.
Bagster, *L. S.*, obituary notice of, 333.
Baker, *J. W.*, synthesis of methyl α-methoxyacrylate and α-methoxyacrylonitrile: characterisation of methoxy-derivatives of propionic acid, 520.
Baker, *J. W.*, and **Hemming**, (*Miss*) *M. L.*, mechanism of aromatic side-chain reactions with reference to polar effects of substituents. Part XI. Aldehydecyanohydrin reaction: evidence for the mesomeric effects of alkyl groups, 191.
Baldwin, *R. R.* See **Bamford**, *C. H.*
Balfe, *M. P.*, **Doughty**, *M. A.*, **Kenyon**, *J.*, and **Poplett**, *R.*, alkyl–oxygen fission in carboxylic esters. Part II. Derivatives of *p*-methoxybenzhydrol, 605.
Balfe, *M. P.*, **Hills**, *H. W. J.*, **Kenyon**, *J.*, **Phillips**, *H.*, and **Platt**, *B. C.*, alkyl–oxygen fission in carboxylic esters. Part I. Esters of αγ-dimethylallyl alcohol and other substituted allyl alcohols, 556.
Balfe, *M. P.*, and **Webber**, *W. C.*, interaction of *p*-cresol and other phenols with chloral and its hydrate, 718.
Balfe, *M. P.* See also **Airs**, *R. S.*
Bamford, *C. H.*, and **Baldwin**, *R. R.*, accurate analysis of gaseous mixtures, 26.
Barber, *H. J.* See **Ashley**, *J. N.*
Barker, *G. R.*, and **Gulland**, *J. M.*, constitution of yeast ribonucleic acid. Part V. Synthesis of yeast adenylic acid, 231.
Barry, *V. C.*, end-group assay for laminarin and similarly constituted polysaccharides, 578.
Barry, *V. C.*, **Dillon**, *T.*, and **McGettrick**, (*Miss*) *W.*, periodic acid as a test for constitution of polysaccharides, 183.
Bassett, *H.*, and **Durrant**, *R. G.*, equilibria and changes in metal hydroxide sols, 277.
Beilenson, *B.*, and **Hamer**, (*Miss*) *F. M.*, thiazinocyanines. Part I. Carbocyanines containing the 2:4-benzthiazine nucleus, 98.
Bell, *R. C.*, and **Briggs**, *L. H.*, *Solanum* alkaloids. Part I. Alkaloid from the fruit of *Solanum aviculare*, 1.
Bell, *R. C.*, **Briggs**, *L. H.*, and **Carroll**, *J. J.*, *Solanum* alkaloids. Part III. Alkaloids from *Solanum auriculatum*, 12.
Bendall, *J. R.*, **Mann**, *F. G.*, and **Purdie**, *D.*, interaction of chloramine-*T* and hydrogen sulphide, phosphine, and arsine, 157.
Bilham, *P.*, and **Kon**, *G. A. R.*, sapogenins. Part XVI. The acids of elemi resin, 544.
Bilham, *P.*, **Kon**, *G. A. R.*, and **Ross**, *W. C. J.*, sapogenins. Part XII. Position of the carboxyl group in triterpenes. Part XIII. Position of the double bond in acids of the β-amyrin group. Part XIV. Constitution of glycyrrhetic acid and its relation to oleanolic acid. Part XV. Siaresinolic acid, 35, 532, 535, 540.
Birch, *A. J.*, and **Robinson**, (*Sir*) *R.*, long-chain acids containing a quaternary carbon atom. Part I., 488.
Bircumshaw, *L. L.*, and **Everdell**, *M. H.*, kinetics of the reaction between copper and iodine in aqueous (potassium iodide) solution. Part I., 598.
Bird, (*Miss*) *M. L.*, and **Challenger**, *F.*, potassium alkaneselenonates and other alkyl derivatives of selenium, 570.
studies in biological methylation. Part IX. Action of *Scopulariopsis brevicaulis* and certain *Penicillia* on salts of aliphatic seleninic and selenonic acids, 574.
Birkinshaw, *J. H.*, and **Bracken**, *A.*, synthesis of compounds related to mould metabolic products. Part I. 3:5-Dihydroxy-2-formylbenzoic acid and 3:5-dihydroxyphthalic acid, 368.
Birtwell, *S.* See **Hodgson**, *H. H.*
Bograchov, *F.* See **Weizmann**, *M.*
Bolton, *K.*, **Cullingworth**, *J. E.*, **Ghosh**, *B. P.*, and **Cobb**, *J. W.*, primary gaseous products of carbonisation, 252.
Bracken, *A.* See **Birkinshaw**, *J. H.*
Bradbury, *F. R.*, and **Linnell**, *W. H.*, chemotherapeutic studies in the acridine series. Part IX. The chloroaminoacridines. 377.
Bramley, *D.*, and **Chamberlain**, *N. H.*, preparation and properties of *p*-thiolbenzoic acid, 376.
Brandon, *T. W.* See **German**, *W. L.*
Briggs, *L. H.*, and **Carroll**, *J. J.*, *Solanum* alkaloids. Part IV. The glycosidic moiety of solauricine, 17.
Briggs, *L. H.*, **De Ath**, *G. C.*, and **Ellis**, *S. R.*, reactions of hydrazoic acid. Part I., 61.
Briggs, *L. H.*, **Newbold**, *R. P.*, and **Stace**, *N. E.*, *Solanum* alkaloids. Part II. Solasonine, 3.
Briggs, *L. H.*, and **Russell**, *W. E.*, *Sophora* alkaloids. Part III. Alkaloids of the seeds of *S. chrysophylla*. Part IV. Alkaloids from the seeds of the Chatham Islands species, 507, 555.
Briggs, *L. H.* See also **Bell**, *R. C.*
Briscoe, *H. V. A.* See **Winter**, *E. R. S.*
Britton, *H. T. S.*, and **Clissold**, (*Miss*) *E. M.*, potentiometric study of the oxidation of phenylhydrazine by cupric ions, including titration of Fehling's solution with phenylhydrazine, 528.
Bunn, *C. W.*, and **Garner**, (*Mrs.*) *E. V.*, crystal structure of rubber hydrochloride, 654.

C.

Cameron, *J. M. L.* See **Preston**, *R. W. G.*
Campbell, *N.*, and **MacLean**, *J. A. R.*, the preparation of 1-substituted carbazoles, 504.
Carroll, *J. J.* See **Bell**, *R. C.*, and **Briggs**, *L. H.*
Carter, *A. H.*, **Race**, *E.*, and **Rowe**, *F. M.*, bromination of 1:5-dihydroxy- and 1:5-diacetoxy-naphthalene, 5-methoxy-1-naphthol, and 1:5-dimethoxynaphthalene, 236.
Case, *T. B.*, obituary notice of, 333.
Challenger, *F.*, **Taylor**, *P.*, and **Taylor**, *B.*, interaction of betaine with primary aromatic amines, organic disulphides, and sodium sulphite, 48.

Challenger, *F.* See also **Bird,** (*Miss*) *M. L.*
Chamberlain, *N. H.* See **Bramley,** *D.*
Clark, *D.*, **Powell,** *H. M.*, and **Wells,** *A. F.*, crystal structure of phosphorus pentachloride, 642.
Clemo, *G. R.*, and **Melrose,** *T. A.*, synthesis of 2-methylpyrrolizidine, 424.
Clemo, *G. R.*, and **Swan,** *G. A.*, molecular dissymmetry due to symmetrically placed hydrogen and deuterium. Part III. Attempted resolution of 4:4′-dibromo-2:3:5:6-tetradeuterobenzhydrylamine; determination of deuterium in organic compounds, 370.
a synthesis of "heavy" *dl*-adrenaline, 395.
Clifton, *J. W.* See **King,** *F. E.*
Clissold, (*Miss*) *E. M.* See **Britton,** *H. T. S.*
Coates, *G. E.*, and **Sutton,** *L. E.*, determination of the angle between the phenyl groups in αα-diphenylethylene, from electric dipole moment measurements, 567.
Coats, *R. R.*, and **Cook,** *J. W.*, azulenes. Part I. Synthesis of vetivazulene, 559.
Cobb, *J. W.* See **Bolton,** *K.*
Cook, *A. H.*, **Garner,** *J.*, and **Perry,** *C. A.*, quinoxaline cyanines. Part I., 710.
Cook, *A. H.*, **Heilbron,** *I. M.*, and **Lewis,** *F. B.*, alkyl quinols and related compounds, 659.
Cook, *J. W.* See **Coats,** *R. R.*
Copp, *F. C.*, and **Simonsen,** *J. L.*, *meso*benzanthronecarboxylic acids, 209.
Cornforth, *J. W.*, **Cornforth,** (*Mrs.*) *R. H.*, and **Robinson,** (*Sir*) *R.*, nuclear methylation of phenols by means of methanolic sodium methoxide, 682.
preparation of β-tetralone from β-naphthol and some analogous transformations, 689.
Cornforth, *J. W.*, and **Robinson,** (*Sir*) *R.*, experiments on the synthesis of substances related to the sterols. Part XL. Preparation of 2:7-dihydroxyphenanthrene and certain derivatives; reduction of 1-γ-ketobutyl-2-naphthol, 684.
Cornforth, (*Mrs.*) *R. H.*, and **Robinson,** (*Sir*) *R.*, preparation of 3-substituted indoles, 680.
Cornforth, (*Mrs.*) *R. H.* See also **Cornforth,** *J. W.*
Cottrell, *T. L.*, and **Percival,** *E. G. V.*, constitution of agar. Part III. Isolation of hepta-acetyl *dl*-galactose from 3:6-anhydro-β-methyl-α-galactoside, 749.
Cullingworth, *J. E.* See **Bolton,** *K.*

D.

Dancaster, *E. A.*, action of sodium silicate on manganous salts in solution, 581.
Davidson, *N. R.*, and **Sutton,** *L. E.*, electric polarisation of mercurous trichloroacetate and of quinol bistrichloroacetate, 565.
Davies, *W. H.*, and **Sexton,** *W. A.*, reactions of benzthiazole derivatives. Part III. Interaction of 1-thiolbenzthiazoles and alcohols, 304.
De Ath, *G. C.* See **Briggs,** *L. H.*
Dewing, *T.*, **Gray,** *W. H.*, **Platt,** *B. C.*, and **Stephenson,** *D.*, anti-bacterial substances allied to sulphanilamide, 239.
Dillon, *T.* See **Barry,** *V. C.*
Dorée, *C.*, and **Pepper,** *A. C.*, erucic acid; preparation of erucic acid; general oxidation reactions; oxidation with gaseous oxygen, 477.
Doughty, *M. A.* See **Balfe,** *M. P.*
Durrant, *R. G.* See **Bassett,** *H.*
Dyson, *G. M.*, and **Harrington,** *T.*, action of chlorine on aryl thiocarbimides and reactions of aryl *iso*cyanodichlorides. Part II. Part III. Addition of chlorine to α-naphthylthiocarbimide and the structure of the compounds obtained, 150, 374.

E.

Earl, *J. C.*, and **Hills,** *N. G.*, diazotisation and nitrosation of amines. Part V. Effect of lowering the dielectric constant of the reaction mixture, 275.
Ellis, *S. R.* See **Briggs,** *L. H.*
Emeléus, *H. J.*, fluorine, 441.
Everdell, *M. H.* See **Bircumshaw,** *L. L.*
Ewins, *A. J.* See **Ashley,** *J. N.*

F.

Fahim, *H.* See **Zaki,** *A.*
Farmer, *E. H.*, and **Michael,** *S. E.*, rubber, polyisoprenes, and allied compounds. Part II. Molecule-linking capacity of free radicals and its bearing on mechanism of vulcanisation and photo-gelling reactions, 513.
Farmer, *E. H.*, and **Narracott,** *E. S.*, autoxidisability of the alkyl groups in xylene, 185.
Farmer, *E. H.*, and **Sundralingam,** *A.*, course of autoxidation reactions in polyisoprenes and allied compounds. Part I. Structure and reactive tendencies of peroxides of simple olefins, 121.
Farmer, *E. H.*, and **Sutton,** *D. A.*, rubber, polyisoprenes, and allied compounds. Part I. Synthesis of low-molecular polyisoprenes of the rubber and the squalene type, 116.
course of autoxidation reactions in polyisoprenes and allied compounds. Part II. Hydroperoxidic structure and chain scission in low-molecular polyisoprenes, 139.
Flintoff, *R. J.*, obituary notice of, 64.
Foster, *C. K.* See **Hodgson,** *H. H.*
Freundlich, *H.*, obituary notice of, 646.

G.

Garner, (*Mrs.*) *E. V.* See **Bunn,** *C. W.*
Garner, *J.* See **Cook,** *A. H.*
Geake, *A.*, obituary notice of, 475.
German, *W. L.*, and **Brandon,** *T. W.*, ionisation in non-aqueous solvents. Part V. Formation of methoxides and ethoxides in methyl and in ethyl alcohol, 526.
Ghosh, *B. P.* See **Bolton,** *K.*
Gibling, *T. W.*, molecular volume and structure. Parts III. and IV., 661.
Gibson, *G. M.*, **Harley-Mason,** *J.*, **Litherland,** *A.*, and **Mann,** *F. G.*, amino-derivatives of pentaerythritol. Part II. Thermal decomposition of tetrahydrochlorides of tetrakismethylaminomethylmethane and of tetrakisdimethylaminomethylmethane, 163.
Gibson, *G. M.*, and **Mann,** *F. G.*, amino-derivatives of pentaerythritol. Part III. Formation and thermal decomposition of quaternary salts of tetrakisdimethylaminomethylmethane, 175.
Gillam, *A. E.*, and **West,** *T. F.*, absorption spectra of terpenoid compounds. Part II. Irone. Part III. Thiosemicarbazones of irone, eucarvone, and related ketones. Part IV. Five-atom ring unsaturated ketones, 95, 483, 486.
absorption spectra and the structures of pyrethrins I and II, 671.
Goldberg, *A. A.*, vital stains. Part I., 713.
isethionic acid, 716.
Gorvin, *J. H.* See **Ayling,** *E. E.*
Goss, *F. R.*, and **Audsley,** *A.*, magnitude of the solvent effect in dipole-moment measurements. Part VI. Induced and mesomeric moments of alkyl halides and halogenobenzenes, 497.
Goss, *F. R.* See also **Audsley,** *A.*
Gray, *W. H.*, and **Platt,** *B. C.*, carboxylic acid derivatives of 4:4′-diaminodiphenylsulphone, 42.
Gray, *W. H.* See also **Dewing,** *T.*
Graymore, *J.*, cyclic methyleneimines. Part IV. Hydrolysis of quaternary compounds; preparation of secondary amines, 29.
Gregg, *S. J.*, resemblance between surface films on solids and on water, 696.
Gulland, *J. M.* See **Allsebrook,** *W. E.*, and **Barker,** *G. R.*

H.

Habeshaw, *J.* See **Hodgson,** *H. H.*
Hamer, (*Miss*) *F. M.* See **Beilenson,** *B.*
Harley-Mason, *J.*, and **Mann,** *F. G.*, comparative reactivity of carbonyl groups in thionaphthenquinones. Part I. Constitution of thioindigoid dyes, 404.
Harley-Mason, *J.* See also **Gibson,** *G. M.*

Harper, *S. H.*, active principles of leguminous fish-poison plants. Part VI. Robustic acid. Part VII. Reduction of elliptone. Part VIII. Synthesis of dehydrotetrahydroelliptone and of dehydrotetrahydromalaccol. Part IX. Synthesis of furano*iso*flavones related to rotenone, 181, 587, 593, 595.
Harrington, *T.* See **Dyson,** *G. M.*
Haworth, *R. D.*, chemistry of the lignan group of natural products, 448.
Haworth, *W. N.*, **Heath,** *R. L.*, and **Peat,** *S.*, constitution of the starch synthesised *in vitro* by the agency of potato phosphorylase, 55.
Heafield, *T. G.*, and **Hunter,** *L.*, associating effect of the hydrogen atom. Part X. N–H–N bond; constitution of benztriazoles, 420.
Heath, *R. L.* See **Haworth,** *W. N.*
Heilbron, *I. M.*, some aspects of algal chemistry, 79.
Heilbron, *I. M.*, **Johnson,** *A. W.*, **Jones,** *E. R. H.*, and **Spinks,** *A.*, polyene series. Part V. Employment of 3-(2′:6′:6′-trimethyl*cyclo*hexenyl)-1-methylcrotonaldehyde for synthesis of vitamin-*A* and analogues, 727.
Heilbron, *I. M.*, **Jones,** *E. R. H.*, and **Koch,** *H. P.*, polyene series. Part VII. Carbinols from propargyl acetal, 735.
Heilbron, *I. M.* See also **Cook,** *A. H.*
Hemming, (*Miss*) *M. L.* See **Baker,** *J. W.*
Hewett, *C. L.*, condensation of aromatic ketones with ethyl succinate, 585.
Hilditch, *T. P.*, and **Plimmer,** *H.*, oxidation of hydroxyketostearic acids in presence of alcoholic alkali, 204.
Hills, *H. W. J.* See **Balfe,** *M. P.*
Hills, *N. G.* See **Earl,** *J. C.*
Hinkel, *L. E.* See **Ayling,** *E. E.*
Hirst, *E. L.*, chemistry of the pectic materials and plant gums, 70.
Hodgson, *H. H.*, **Birtwell,** *S.*, and **Walker,** *John*, interpretation of the Sandmeyer reaction. Part II. Corrections. Part III. Evidence in favour of a mechanism involving anionoid halogen, 376, 720.
Hodgson, *H. H.*, and **Foster,** *C. K.*, decomposition of arylazo-β-naphthylamines by sodium nitrite and glacial acetic acid, 30.
some reactions of the diazonium salts of arylazo-β-naphthylamines, 435.
decomposition of zinc chloride double salts of diazonium compounds by alcohols and phenol, 581.
preparation of 2:3:5:6-tetrabromobenzoquinone, 583.
influence of *p*-substituents on decomposition of zinc chloride double salts of diazonium chlorides by acetic anhydride, 747.
Hodgson, *H. H.*, and **Habeshaw,** *J.*, exchange reactions of 4-nitro-1-naphthyl methyl ether and 4-nitro-1-naphthyl ethyl ether with sodium ethoxide and methoxide respectively, and the reduction of certain 1-nitronaphthalene derivatives, 45.
Hodgson, *H. H.*, **Leigh,** *E.*, and **Turner,** *G.*, preparation of symmetrical azo-compounds, positional influence of the nitro-group on decomposition of nitronaphthalenediazonium sulphates by cuprous hydroxide, and production of 2-nitronaphthalene, 744.
Hodgson, *H. H.*, and **Nicholson,** *D. E.*, preparation of 2-iodobenzoquinone, 375.
Hodgson, *H. H.*, and **Turner,** *G.*, coupling of *m*-halogenophenols with diazotised aniline, and the existence of chromoisomerism among the 3-halogeno-4-benzeneazophenols, 433.
interaction of dimethylaniline and nitric acid, 584.
Hodgson, *H. H.*, and **Turner,** *H. S.*, influence of the 5-nitro-group on the halogenation and nitration of 5-nitro-1-naphthylamine and of some related naphthalides, 723.
action of cuprous oxide on diazotised amines in ethyl-alcoholic acid solution, 748.
Holliman, *F. G.*, and **Mann,** *F. G.*, synthetic application of *o*-β-bromoethylbenzyl bromide. Part I. Sulphanilamide derivatives of 1:2:3:4-tetrahydro*iso*quinoline, 737.
Hopkins, *G.*, and **Hunter,** *L.*, associating effect of the hydrogen atom. Part XI. Hydrogen bonds involving the sulphur atom; S–H–N bond, 638.
Hudson, *B. J. F.*, and **Robinson,** (*Sir*) *R.*, decalin-1:5-dione and 2:2′-diketodi*cyclo*pentyl, 691.
Hunter, *L.* See **Heafield,** *T. G.*, and **Hopkins,** *G.*

I.

Irwin, *M.* See **Airs,** *R. S.*
Iskander, *Y.* See **Schönberg,** *A.*
Ismail, *A. F. A.* See **Schönberg,** *A.*

J.

Jamison, (*Miss*) *M. M.*, and **Turner,** *E. E.*, inter-relation of first- and second-order asymmetric transformations, 437.
separation of diastereoisomerides by selective adsorption on optically inactive material, 611.
Johnson, *A. W.* See **Heilbron,** *I. M.*
Jones, *B.*, halogenation of phenolic ethers and anilides. Part XII. Arrhenius activation energies. Part XIII. Arrhenius activation energies for di- and poly-substituted aromatic ethers, 418, 676.
Jones, *E. R. H.*, and **Koch,** *H. P.*, self-condensation of acetyl*cyclo*hexene, 393.
Jones, *E. R. H.*, and **McCombie,** *J. T.*, polyene series. Part VI. Preparation of ethinylcarbinols from αβ-unsaturated aldehydes, 733.
Jones, *E. R. H.*, **Wilkinson,** *P. A.*, and **Kerlogue,** *R. H.*, studies in the sterol group. Part XLIV. Oxidation of phytosterols with the Oppenauer reagent, 391.
Jones, *E. R. H.* See also **Heilbron,** *I. M.*
Jones, *W. G. M.*, and **Peat,** *S.*, constitution of agar, 225.

K.

Kelly, *D. F.*, **O'Connor,** (*Miss*) *M. J.*, and **Reilly,** *J.*, azeotrope of nicotine and water, 511.
Kenyon, *J.* See **Airs,** *R. S.*, and **Balfe,** *M. P.*
Kerlogue, *R. H.* See **Jones,** *E. R. H.*
Kermack, *W. O.*, and **Weatherhead,** (*Miss*) *A. P.*, some anilinopyridine derivatives, 726.
Kermack, *W. O.*, and **Webster,** *W.*, attempts to find new antimalarials. Part XVIII. Derivatives of *m*-phenanthroline, 213.
King, *F. E.*, **Clifton,** *J. W.*, and **Openshaw,** *H. T.*, synthesis of ethyl 1-methylpyrrolidine-2-acetate, 422.
King, *F. E.*, and **King,** *T. J.*, synthesis of phthalides from 3:4:5-trimethoxybenzoic acid, 726.
King, *F. E.*, and **Sherred,** *J. A.*, preparation of 8-hydroxyquinoline, 415.
King, *G.*, peroxides derived from η-aldehydo-octoic acid and nonaldehyde: bis-α-hydroxy-ω-carboxyoctyl peroxide and bis-α-hydroxynonyl peroxide, 218.
the dihydroxystearic acid of castor oil; its constitution and structural relationship to 9:10-dihydroxystearic acids, m.ps. 132° and 95°, 387.
King, *H.*, *iso*oxazolidine and tetrahydro-1:2-*iso*oxazine, 432.
King, *H.*, and **Work,** *T. S.*, antiplasmodial action and chemical constitution. Part V. Carbinolamines derived from 6-methoxyquinoline, 401.
King, *T. J.* See **King,** *F. E.*
Knaggs, (*Miss*) *I.*, and **Lonsdale,** (*Mrs.*) *K.*, crystal structure of *trans-trans*-methyl fumarate and *trans-trans*-methyl muconate, 417.
Koch, *H. P.* See **Heilbron,** *I. M.*, and **Jones,** *E. R. H.*
Kon, *G. A. R.*, and **Ross,** *W. C. J.*, sapogenins. Part XVII. Position of the carboxyl group in oleanolic and glycyrrhetic acids, 741.
Kon, *G. A. R.* See also **Bilham,** *P.*

L.

Leaf, *G.*, **Todd,** *A. R.*, and **Wilkinson,** *S.*, *Cannabis indica*. Part IX. Isolation of 3′:4′:5′:6′-tetrahydrodibenzopyran derivatives from pulegone–orcinol and pulegone–olivetol condensation products; *d*-tetrahydrocannabinol, 185.
Leigh, *E.* See **Hodgson,** *H. H.*
Lewis, *F. B.* See **Cook,** *A. H.*
Linnell, *W. H.* See **Bradbury,** *F. R.*
Lisle, *E. B.*, colour test for carcinogenic hydrocarbons, 584.
Litherland, *A.* See **Gibson,** *G. M.*
Lonsdale, (*Mrs.*) *K.* See **Knaggs,** (*Miss*) *I.*

Lyon, *D. R.*, and **Mann**, *F. G.*, tetra-aryl-phosphonium, -arsonium and -stibonium salts. Part II. Mechanism of their formation by the aluminium chloride reaction, 666.

M.

McCombie, *J. T.* See **Jones**, *E. R. H.*
McGettrick, (*Miss*) *W.* See **Barry**, *V. C.*
McKeown, *A.*, obituary notice of, 476.
McLean, *J.*, and **Muir**, *G. D.*, reactions of thiazoles and glyoxalines with picryl chloride and 2:4-dinitrochlorobenzene, 383.
Macnab, *W.*, obituary notice of, 64.
Madinaveitia, (*Mrs.*) *A.*, **Russell**, *P. B.*, and **Todd**, *A. R.*, *Cannabis indica*. Part XI. Examination of the alkali-soluble portion of American hemp resin, 628.
Mann, *F. G.* See **Bendall**, *J. R.*, **Gibson**, *G. M.*, **Harley-Mason**, *J.*, **Holliman**, *F. G.*, and **Lyon**, *D. R.*
Marais, *J. L. C.* See **Backeberg**, *O. G.*
Marsh, *J. K.*, rare-earth metal amalgams. Part I. Reaction between sodium amalgam and rare-earth acetate and chloride solutions. Part II. Separation of neodymium, samarium, and gadolinium, 398, 523.
Melrose, *T. A.* See **Clemo**, *G. R.*
Menon, *B. K.*, **Menon**, *E. V.*, and **Peacock**, *D. H.*, nitration of 9-*p*-toluenesulphonylcarbazole, 509.
Menon, *E. V.* See **Menon**, *B. K.*
Metcalf, *W. S.*, absorption spectra of mono-, di-, and trichloroamines and some aliphatic derivatives, 148.
Michael, *S. E.* See **Farmer**, *E. H.*
Miller, *W. L.*, obituary notice of, 334.
Mills, *W. H.*, the basis of stereochemistry, 457.
Mohrhenn, *H. G. G.*, obituary notice of, 65.
Morice, (*Miss*) *I. M.*, and **Simpson**, *J. C. E.*, the triterpene group. Part IX. Constitution of breïn and maniladiol, 198.
Muir, *G. D.* See **McLean**, *J.*

N.

Narracott, *E. S.* See **Farmer**, *E. H.*
Nelson, *W. A. G.*, and **Percival**, *E. G. V.*, studies on seed mucilages. Part II. Seed mucilage of *Plantago arenaria*, 58.
Newbery, *G.* See **Ashley**, *J. N.*
Newbold, *R. P.* See **Briggs**, *L. H.*
Nicholson, *D. E.* See **Hodgson**, *H. H.*

O.

O'Connor, (*Miss*) *M. J.* See **Kelly**, *D. F.*
Openshaw, *H. T.* See **King**, *F. E.*
Ormandy, *W. R.*, obituary notice of, 66.
Oxford, *A. E.*, synthesis and anti-bacterial properties of alkyl and alkenyl derivatives of 2:6-dimethoxybenzoquinone, 577.
preparation of 4:6-dimethoxytoluquinone, 583.

P.

Peacock, *D. H.* See **Menon**, *B. K.*
Peat, *S.* See **Haworth**, *W. N.*, and **Jones**, *W. G. M.*
Penfold, *A. R.*, and **Simonsen**, *J. L.*, 1:3:3-trimethyl-Δ^1-*cyclo*hexene-4-carboxylic acid: its formation from *l*-Δ^3-carene-5:6-epoxide, 206.
Pepper, *A. C.* See **Dorée**, *C.*
Percival, *E. G. V.*, and **Thomson**, *T. G. H.*, studies on agar-agar. Part IV., 750.
Percival, *E. G. V.* See also **Cottrell**, *T. L.*, and **Nelson**, *W. A. G.*
Perry, *C. A.* See **Cook**, *A. H.*
Peters, *A. T.*, acenaphthene series. Part I. Mono- and di-*tert.*-butyl-acenaphthene, -acenaphthenequinone, and -naphthalic anhydride, and their derivatives, 562.
Petrow, *V. A.*, new syntheses of heterocyclic compounds. Part I. 2:3-Dialkylquinolines, 693.
Phillips, *H.* See **Balfe**, *M. P.*
Phillips, *M. A.*, crotonic acid series. Part II. Nitrogen derivatives of α-phenylcrotonic acid, 220.
Phillips, *M. A.*, and **Shapiro**, *H.*, preparation of 2-thiolpyridine derivatives, 584.
Platt, *B. C.* See **Balfe**, *M. P.*, **Dewing**, *T.*, and **Gray**, *W. H.*
Plimmer, *H.* See **Hilditch**, *T. P.*
Pond, *J. A.*, obituary notice of, 476.
Poplett, *R.* See **Balfe**, *M. P.*
Pound, *J. R.*, determination of hypophosphites by potassium permanganate, 307.
Powell, *H. M.* See **Clark**, *D.*
Preston, *R. W. G.*, **Tucker**, *S. H.*, and **Cameron**, *J. M. L.*, the Graebe–Ullmann synthesis of carbazole derivatives; preparation and synthesis of 1-nitrocarbazole, 500.
Purdie, *D.* See **Bendall**, *J. R.*

R.

Race, *E.* See **Carter**, *A. H.*
Rapson, *W. S.*, and **Shuttleworth**, *R. G.*, benzcyclooctatetraenes. Part II. Action of acetic anhydride on δ-benzylidene-lævulic acids, 33.
Rayleigh, (*Lord*), Sir Joseph J. Thomson, 467.
Reilly, *J.* See **Kelly**, *D. F.*
Roberts, *K. C.*, caoutchol component of natural rubber, 223.
Robinson, (*Sir*) *R.* See **Birch**, *A. J.*, **Cornforth**, *J. W.*, **Cornforth**, (*Mrs.*) *R. H.*, and **Hudson**, *B. J. F.*
Robison, *R.*, obituary notice of, 67.
Ross, *W. C. J.* See **Bilham**, *P.*, and **Kon**, *G. A. R.*
Rowe, *F. M.* See **Carter**, *A. H.*
Russell, *P. B.* See **Madinaveitia**, (*Mrs.*) *A.*
Russell, *W. E.* See **Briggs**, *L. H.*

S.

Schönberg, *A.*, and **Asker**, (*Miss*) *W.*, cleavage of the ethylene linkage by the action of sulphur, 272.
cleavage of the ethylene linkage by the action of thionyl chloride, 725.
Schönberg, *A.*, and **Iskander**, *Y.*, organic sulphur compounds. Part XXVII. Relation between the constitution of thioethers and thiols and their sensitivity towards alkali, 90.
Schönberg, *A.*, and **Ismail**, *A. F. A.*, preparation of 1:2:4:5-tetraphenylbenzene from benzylideneacetophenone, 585.
Selt, *A. D. H.* See **Ashley**, *J. N.*
Sexton, *W. A.*, condensation of *o*-phenylenediamine with ethyl acetoacetate, 303.
Sexton, *W. A.* See also **Davies**, *W. H.*
Shapiro, *H.* See **Phillips**, *M. A.*
Sherred, *J. A.* See **King**, *F. E.*
Shuttleworth, *R. G.* See **Rapson**, *W. S.*
Simonsen, *J. L.*, and **Todd**, *A. R.*, *Cannabis indica*. Part X. Essential oil from Egyptian hashish, 188.
Simonsen, *J. L.* See also **Copp**, *F. C.*, and **Penfold**, *A. R.*
Simpson, *J. C. E.*, and **Stephenson**, *O.*, cinnolines. Part I. Some new examples, 353.
Simpson, *J. C. E.* See also **Morice**, (*Miss*) *I. M.*
Spinks, *A.* See **Heilbron**, *I. M.*
Stace, *N. E.* See **Briggs**, *L. H.*
Stacey, *M.*, and **Woolley**, *J. M.*, nature of the carbohydrate residue in ovomucoid. Part II., 550.
Stephenson, *D.* See **Dewing**, *T.*
Stephenson, *O.* See **Simpson**, *J. C. E.*
Story, *L. F.* See **Allsebrook**, *W. E.*
Sully, *B. D.*, standardisation of sodium thiosulphate with potassium dichromate, 366.
Sundralingam, *A.* See **Farmer**, *E. H.*
Sutton, *D. A.* See **Farmer**, *E. H.*
Sutton, *L. E.* See **Coates**, *G. E.*, and **Davidson**, *N. R.*
Swain, *G.*, and **Todd**, *A. R.*, indeno-2″:3″:2′:1′-benzanthrone, 626.
Swan, *G. A.* See **Clemo**, *G. R.*

T.

Taylor, *B.* See **Challenger**, *F.*
Taylor, *P.* See **Challenger**, *F.*
Thomson, *T. G. H.* See **Percival**, *E. G. V.*

Thorne, *L. T.*, obituary notice of, 336.
Todd, *A. R.* See **Leaf**, *G.*, **Madinaveitia**, (*Mrs.*) *A.*, **Simonsen**, *J. L.*, and **Swain**, *G.*
Tucker, *S. H.* See **Preston**, *R. W. G.*
Turner, *E. E.* See **Jamison**, (*Miss*) *M. M.*
Turner, *G.* See **Hodgson**, *H. H.*
Turner, *H. S.* See **Hodgson**, *H. H.*

W.

Walker, *James*, experiments on the synthesis of potential cortical hormone substitutes; hydroxy-carbonyl derivatives of diphenyl ether and related compounds, 347.
Walker, *John.* See **Hodgson**, *H. H.*
Walsh, *E. O'F.*, preparation of 1-*p*-aminobenzenesulphonamide-2:5-dimethylpyrrole, 726.
Wassermann, *A.*, mechanism of additions to double bonds. Part XIV. Nature of the activated complex in bimolecular diene syntheses, 612.
homogeneous catalysis of diene syntheses; new type of third-order reaction, 618.
solvent effects in association equilibria, 621.
homogeneous catalysis and solvent effects in a diene synthesis, 623.
Waters, *W. A.*, mechanisms of covalent-bond fission, 153.
decomposition reactions of aromatic diazo-compounds. Part X. Sandmeyer reaction, 266.
Weatherhead, (*Miss*) *A. P.* See **Kermack**, *W. O.*
Webber, *W. C.* See **Balfe**, *M. P.*
Webster, *W.* See **Kermack**, *W. O.*
Weiss, *J.*, formation and structure of organic molecular compounds, 245.
Weizmann, *M.*, and **Bograchov**, *F.*, derivatives of 1′-aza-3:4-benzpyrene, 377.
Wells, *A. F.* See **Clark**, *D.*
West, *T. F.* See **Gillam**, *A. E.*
Whitelegg, *H. H.*, obituary notice of, 69.
Wilkinson, *P. A.* See **Jones**, *E. R. H.*
Wilkinson, *S.* See **Leaf**, *G.*
Williams, *G.*, and **Wilson**, *C. L.*, reactions of furan compounds. Part I. Constitution of the coloured condensation product from furfural, aniline, and aniline hydrochloride, 506.
Williams, *R. T.*, 5-amino-2-hydroxybenzenesulphonamide and some related compounds, 708.
Wilson, *C. L.* See **Williams**, *G.*
Winter, *E. R. S.*, and **Briscoe**, *H. V. A.*, the interchange of heavy oxygen between water and inorganic oxy-anions, 631.
Woolley, *J. M.* See **Stacey**, *M.*
Work, *T. S.*, antiplasmodial action and chemical constitution. Part VI. Compounds related to lepidylamine, 426.
synthesis of amines from amides through the amidodichlorides, 429.
Work, *T. S.* See also **King**, *H.*
Wright, *R.*, automatic adjustment of solute concentration in the "moving-boundary" method for determination of transport numbers, 678.
Wright, (*Mrs.*) *W. G.*, compounds of naphthoic acids with their copper and nickel salts; copper and nickel sulphinates and their oxidation to sulphonates, 263.

Z.

Zaki, *A.*, and **Fahim**, *H.*, derivatives of *β*-*o*-methoxyphenylpropaldehyde, 182.
quaternary ammonium salts and their decomposition products, 270.
preparation of *p*-alkyl-substituted benzoic acids, 307.

INDEX OF SUBJECTS, 1942.

A.

Acenaphthene series, 562.
Acetic acid, *tri*chloro-, mercurous and quinol salts, electric polarisation of, 565.
Acetoacetic acid, ethyl ester, condensation of, with *o*-phenylenediamine, 303.
Acetoacet-*o*-nitroanilide, 304.
Aceto-1-naphthalide, 2-bromo-5-nitro-, 2:4-*di*bromo-5-nitro-, 2:4-*di*chloro-5-nitro-, and 2-iodo-5-nitro-, 724.
Acetonyltrimethylammonium picrate, 174.
Acetophenone, 4-bromo-3:5-*di*nitro-, 501.
2′-Acetoxymercuri-3′-hydroxybenzylidenesulphanilamide, 242.
9-Acetylcarbazole, 3-cyano-, and 1-nitro-, 502.
N^4-Acetyl-N^1-(6-chlorolepidyl)sulphanilamide, 429.
Acetyldehydrodeoxoglycyrrhetic acid, methyl ester, 539.
Acetyldihydro-α-elemolic acid, methyl ester, 549.
Acetylelliptic acid, and its ethyl ester, 592.
Acetyl*cyclo*hexene, self-condensation of, 393.
Acetyl-21-keto-oleanolic acid, methyl ester, 543.
12-Acetyl-9-ketotetradecahydrophenanthrenes, and their derivatives, 394.
***O*-Acetylmandelylisethionic acid,** sodium salt, 718.
N^4-Acetyl-N^1-(6-methoxylepidyl)sulphanilamide, 428.
1-(*m*-Acetylphenyliminomethyl)*cyclo*hexan-2-one, 696.
β-(2-Acetyl-4-*iso*propyl*cyclo*pentyl)butyric acid, and its derivatives, 562.
Acetylsiaresinolic acid, methyl ester, 543.
Acetyl-1:2:3:4-tetrahydroacridine, and its picrate, 696.
Acids, carboxylic esters, alkyl–oxygen fusion in, 556, 605.
long-chain, with quaternary carbon, 488.
Acridines, chloroamino-, and chloronitro-, 377.
Acridine series, chemotherapy in, 377.
Acridine-7-sulphonamide, 2-amino-, and 2-nitro-, 183.
Acridone, 8-chloro-2-amino-, 6-chloro-3-nitro-, and 8-chloro-2-nitro-10-hydroxy-, 380.
***dl*-Adrenaline,** "heavy," synthesis of, 395.
Agar-agar, constitution of, 225, 749.
studies on, 750.
Alcohols, reactions of, with 1-thiolbenzthiazoles, 304.
Aldehydes, cyanohydrin reaction with, 191.
αβ-unsaturated, conversion of, into ethinylcarbinols, 733.
η-Aldehydo-octoic acid, peroxide from, 218.
Algæ, chemistry of, 79.
Alkyl halides, dipole moments of, 497.
iodides, dipole moments of, 358.
***p*-Alkylbenzoic acids,** preparation of, 307.
Alkylquinols, and their derivatives, 659.
Alkylseleninic acids, salts, action on, of moulds, 574.
Alkylselenonic acids, potassium salts, 570.
salts, action on, of moulds, 574.
Aluminium hydroxide, sols, 287.
Amalgams. See Mercury alloys.
4-Amidino-2′-cyanodiphenyl, 110.
4-Amidinodiphenyl ether, 110.
4-Amidinomethylbenzamidine *di*hydrochloride, 110.
4-Amidinomethylphenyl 4-amidinobenzyl ether, 110.
Amidinophenyl 4-amidinobenzyl ether ***di*hydrochlorides,** 110.
4-Amidinophenyl 4-amidino-β-phenylethyl ether ***di*hydrochloride,** 110.
4-Amidinostilbene, hydrochloride, 110.
4′-Amidinostilbene, 4-amino-, 112.
4-amino-, and 4-nitro-, hydrochlorides, 110.
Amines, aromatic primary, reactions of, with betaine, 48.
diazotisation and nitrosation of, 275.
diazotised, action of cuprous oxide on, in ethyl-alcoholic acid solution, 748.
secondary, preparation of, 29.
synthesis of, from amides, 429.
Amines, *mono-*, *di-*, and *tri*-chloro, spectra of, absorption, 148.
Ammonium organic compounds, quaternary, 270.
***tert.*-Amyl** fluoride, 499.
***n*-Amyl β-*n*-amyl*iso*propenyl ketone,** 496.
***p*-*n*-Amylbenzoic acid,** 308.
***n*-Amylhexylamine,** and its hydrochloride, 403.
***p*-*n*-Amylphenyl methyl ketone,** and its derivatives, 308.
α- and β-**Amyrins,** derivatives of, 202.
β-Amyrin group, acids of, structure of, 532.
Anilides, halogenation of, 418, 676.
Aniline, condensation of, with its hydrochloride and furfural, 506.
2-Anilino-5-hydroxy-1:4-naphthaquinone, 6-bromo-, 238.
2-Anilinonicotinic acid, 726.
4-Anilinopyridine, 726.
2-Anilinovinylquinoline methiodide, 712.
***p*-Anisidinoaceto-*p*-anisidide,** and *N*-nitroso-, 54.
2-*p*-Anisidinonicotinic acid, 726.
Annual General Meeting, 309.
Anthracite, carbonisation of, 256.
Antimalarials, 213.
Antiplasmodial action and constitution, 401, 426.
Arsenic *tri*hydride, reaction of, with chloramine-*T*, 157.
1-(4′-Arsonobenzeneazo)-2-amino-8-naphthol-3:6-disulphonic acid, *tetra*potassium salt, 715.
2-(4′-Arsonobenzeneazo)-1-amino-8-naphthol-3:6-disulphonic acid, 2-2′:6′-*di*iodo-, *tetra*sodium salt, 715.
Aryl *iso*cyano*di*chlorides, reactions of, 150, 374.
thiocarbimides, action of chlorine on, 150, 374.
Arylazo-β-naphthylamines, decomposition of, by acetic acid and sodium nitrite, 30.
diazonium salts, reactions of, 435.
Asymmetric transformations, first- and second-order, 437.
1′-Aza-3:4-benzpyrene, derivatives of, 377.
γ-Azatrimethin[2-(3-ethyldihydrobenzthiazole)][3-(2:4-benzthiazine)], 102.
Azobenzene, 4:4′-*di*amino-, and -*di*cyano-, 112.
Azo-compounds, symmetrical, preparation of, 744.
Azoimide, reactions of, 61.
1:1′-Azonaphthalene, 2:2′-*di*chloro-, and 5:5′-*di*nitro-, 746.
4:4′-*di*chloro-, 47.
2:2′-Azonaphthalene, 1:1′-*di*chloro-, 746.
Azulenes, 559.

B.

Bakelite, carbonisation of, 254.
Balance sheets, 321.
Behenic acid, 13:14-*di*hydroxy-, methyl ester, 482.
Benzanilide, 4:4′-*di*cyano-, 115.
***meso*Benzanthrone,** 9-amino-, and its acetyl derivative, and 9-chloro-, 211.
***meso*Benzanthronecarboxylic acids,** and their esters, 209.
Benzene, halogeno-derivatives, dipole moments of, 497.
2-Benzeneazo-6-ethoxylepidine, 383.
2-Benzeneazo-6-methoxylepidine, 383.
4-Benzeneazo-3- and -8-methoxyquinaldines, 382.
Benzeneazonaphthalene, 2-bromo-1-3′-chloro-, and 2-bromo-1-2′:5′-*di*chloro-, 437.
4-Benzeneazophenol, 3-bromo-, and 3-iodo-, 435.
Benzenesulphonamide, *p*-nitro-, 244.
Benzenesulphinic acid, *p*-nitro-, esters, 244.
Benzenesulphonamide, 5-amino-2-hydroxy-, and its acetyl derivative, 708.
1-Benzenesulphonamido-2:5-dimethylpyrrole, 1-*p*-amino-, 726.
4-Benzenesulphonamido-4′-nitrodiphenyl sulphide, 4-*p*-nitro-, 244.
Benzenesulphonanilide, aminohydroxy-derivatives, diacetyl derivatives, 709.
4:4′-*di*cyano-, 115.
Benzenesulphonhydrazide, *p*-amino-, and *s*-*di*-*p*-amino-, and its diacetyl derivative, 740.

Benzenesulphonic acid, aminohydroxy-derivatives, diacetyl derivatives, pyridine salts, 709.
Benzenesulphon-4′-nitroanilide, 4-nitro-, 244.
Benzenesulphon-1-(1:2:3:4-tetrahydroquinolyl)amide, *p*-amino-, acetyl derivative, 740.
Benzenesulphonyl chlorides, aminohydroxy-, diacetyl derivatives, 709.
Benzhydrol, 4:4′-*di*cyano-, 111.
Benzhydrylamine, 4:4′-*di*bromo-, and its hydrochloride, 372.
β-(Benzhydrylthio)propionic acid, 95.
Benzidine-2:2′-disulphonic acid, 5:5′-*di*iodo-, disodium salt, 716.
Benzil, structure of, 661.
Benziminazole-2-acetone, 304.
Benz*cyclo*octatetraenes, 33.
Benzoic acid, *p*-thiol-, preparation and properties of, 376.
Benzophenone, 5-chloro-2-amino-4′-hydroxy-, 3-*mono*- and 2:5-*di*-chloro-4′-hydroxy-, and their derivatives, 356.
4:4′-*di*cyano-, and its phenylhydrazone, 111.
Benzoquinone, compound of, with *cyclo*pentadiene, 623.
Benzoquinone, 2:3:5:6-*tetra*bromo-, preparation of, 583.
2-iodo-, preparation of, 375.
Benz*iso*oxazolidide, 3:5-*di*nitro-, 433.
Benzoyl chloride, 4-cyano-, 115.
α-(Benzoylbenzhydrylthio)acetic acid, 94.
α-Benzoylbenzhydrylthiol, 94.
β-(Benzoylbenzhydrylthio)propionic acid, 94.
β-Benzoyl-αα-diphenylhydrazyl, equilibrium of, with dibenzoyltetraphenyltetrazan, 621.
2:4-Benzthiazine, 3-amino-, and its ethiodide, 101.
Benzthiazole, derivatives, reactions of, 304.
Benzthiazoles, 1-thiol-, reactions of, with alcohols, 304.
Benzthioindigos, 411.
Benzthioindirubins, 411.
Benzthionaphthenindole-indigos, 414.
6:7-Benzthionaphthenquinone-2-*p*-hydroxyanil, 410.
Benzthio-oxindole-3-aldehydes, and their derivatives, 414.
Benztriazoles, constitution of, 420.
Benzyl alcohol, 4-cyano-, and its phenylurethane, 114.
Benzyl ethyl ether, *o*-bromo-, 739.
Benzyl-*n*-amylhexylamine, 403.
Benzyl-*n*-butylhexylamine, 402.
Benzyldiethylnonylammonium iodide, 403.
Benzyldimethylnonylammonium iodide, 403.
Benzyldinonylamine, 403.
Benzylethylhexylamine, 403.
Benzylethylnonylamine, 403.
Benzyl-*n*-hexylamine, preparation of, 402.
Benzylideneacetophenone, 4:4′-*di*cyano-, 113.
4-Benzylideneaminobenzenesulphonylglycine, 242.
δ-Benzylidenelævulic acids, action of acetic anhydride on, 33.
Benzylidenenonylamine, 403.
3-Benzylindole, 682.
α-Benzyl-α-methylacetone *di*nitrophenylhydrazone, 63.
Benzyl-*n*-nonylamine, and its hydrochloride, 403.
Benzyl-*n*-propylhexylamine, 403.
Benzyl-*n*-propylnonylamine, 403.
α-Benzylthioacetic acid, α-*p*-amino-, 92.
α-*p*-nitro-, 92.
β-Benzylthiopropionic acid, β-*p*-nitro-, 92.
Betaine, reactions of, with aromatic amines, organic sulphides, and sodium sulphite, 48.
Biological methylation. See under Methylation.
2:3-Bisbenzamido-1-methyl*cyclo*propane, 174.
2:4-Bisbenzeneazophenol, 3-bromo-, 3-chloro-, and 3-iodo-, 434.
Bis(benzenesulphonmethylamidomethyl)methylamine, 30.
4:4′-Biscamphorimidodiphenylsulphone, 45.
4:4′-Biscarbethoxyformamidodiphenylsulphone, 43.
4:4′-Bis-δ-carbethoxyvaleramidodiphenylsulphone, 44.
4:4′-Bis-η-carbomethoxyoctamidodiphenylsulphone, 44.
4:4′-Biscarboxyacetamidodiphenylsulphone, 43.
4:4′-Bis-*o*-carboxybenzamidodiphenylsulphone, 45.
4:4′-Biscarboxyformamidodiphenylsulphone, 43.
4:4′-Bis-η-carboxyoctamidodiphenylsulphone, 44.
4:4′-Bis-β-carboxypropionamidodiphenylsulphone, 44.
3:6-Bis*tri*chloroacetylcarbazole, 1-nitro-, 503.
Bis-αγ-dimethylallyl ether, 559.
αγ-Bisdimethylamino-β-ethoxy-β-methylpropane, and its dimethiodide, 172.
ββ-Bisdimethylaminomethyl-*N*-methyltrimethyleneimine methiodides, 178.
αγ-Bisdimethylamino-β-methylpropane, and its derivatives, 171.
αγ-Bisdimethylamino-β-methylpropane, β-chloro-, and its derivatives, 172.
αγ-Bisdimethylamino-β-methyl*iso*propyl alcohol, and its derivatives, 171.
αγ-Bisdimethylamino*iso*propyl alcohol, and its methiodide, 172.
Bis-2-(1:3-dimethylquinoxaline)trimethincyanine, 713.
Bis-α-hydroxy-ω-carboxyoctyl *per*oxide, 218.
Bis-α-hydroxynonyl *per*oxide, 218.
αγ-Bismethylaminopropane, and its derivatives, 168.
Bis-(α-naphthylthiocarbimide) oxide, 375.
4:4′-Bis-(*p*-nitrobenzamido)diphenylsulphone, 242.
αβ-Bis-(4-phenylbenzamidrazino)ethylene, and its dihydrochloride, 111.
NN′-**Bis-(α-phenylbutyryl)carbamide**, 223.
Bis-2-(1-phenyl-3-methylquinoxaline)trimethincyanine, and its salts, 713.
4:4′-Bisphthalimidodiphenylsulphone, 44.
1:8-Bispiperidinomethylphenanthrene, 2:7-*di*hydroxy-, 684.
4:4′-Bis-succinimidodiphenylsulphone, 44.
αγ-Bistrimethylammonium-β-methylpropenylene *di*iodide, 172.
β-Boswellanic acid, methyl ester, 41.
Brassidic acid, preparation of, 481.
Brassylic semialdehyde, and its derivatives, 482.
Breienediolone, and its diacetate, 202.
Breienedione, and its derivatives, 201.
Breieneonols, and their acetates, 202.
Brein, constitution of, 198.
Butadiene, bimolecular dimerisation of, 612.
***iso*Butenylethinylcarbinol**, and its derivatives, 735.
3-*tert.*-Butylacenaphthene, and its picrate, 563.
3-*tert.*-Butylacenaphthenequinone, 564.
***p*-*n*-Butylbenzoic acid**, 308.
3-*iso*Butyl-4:6-dimethoxytoluquinone, 578.
***n*-Butylhexylamine**, and its hydrochloride, 402.
Butylhexylaminomethyl-6-methoxy-4-quinolylcarbinol, and its dipicrate, 404.
1-Butyl-2-hydroxy-1:2:3:4-tetrahydronaphthalene, 1-γ-hydroxy-, 688.
3-*n*-Butylindole, 682.
4-*tert.*-Butylnaphthalic acid, derivatives of, 563.
4-*tert.*-Butylphenyl *p*-nitrobenzyl ether, 2-chloro-, 678.
***p*-*n*-Butylphenyl methyl ketone**, and its derivatives, 308.
3′-*tert.*-Butyl-1:7′-thionaphthenacenaphthenylindigo, 564.
***iso*Butyric acid**, β-bromo-, methyl ester, 425.

C.

Cannabidiol, bis-*p*-carboxymethoxybenzoate, 630.
Cannabinol, *p*-carboxymethoxybenzoate, 630.
Cannabis indica, 185, 188, 628.
Caoutchol, 223.
4-Carbamidobenzyl alcohol, 114.
Carbazole, derivatives, synthesis of, Graebe–Ullmann, 500.
Carbazole, 1-amino-, benzoyl derivative, 510.
1-ω-bromoamino-, acetyl derivative, 505.
3-*mono*- and 3:6-*di*-cyano-, and 1- and 3-nitro-, 501.
Carbazoles, 1-substituted, 504.
Carbazole-3:6-dicarboxylic acid, and 1-nitro-, and their ethyl esters, 503.
Carbethoxymethyl-β-carbethoxy-*n*-propylamine, and its picrolonate, 426.
***N*-Carbethoxy*iso*oxazolidine**, 433.
1-(Carbethoxyphenyliminomethyl)*cyclo*hexan-2-ones, 696.
β-Carbethoxy-*n*-propylamine, and its picrate, 425.
Carbethoxy-1:2:3:4-tetrahydroacridines, and their picrates, 696.
***N*-Carbethoxytetrahydro*iso*oxazine**, 433.
Carbocyanines containing 2:4-benzthiazine nucleus, 98.
Carbocyclic compounds, parachors of, 661.
1-(*o*-Carbomethoxyphenyliminomethyl)*cyclo*hexan-2-one, 696.
Carbonisation, gaseous products of, 252.
4′-*o*-Carboxybenzamidodiphenylsulphone, 4-amino-, 45.
6′-(Carboxybenzeneazo)-1-amino-8-naphthol-3:6-disulphonic acid, 2-2′:4′-*di*iodo-, *tri*sodium salt, 716.
4′-Carboxyformamidodiphenylsulphone, 4-amino-, 43.
3-Carboxynaphthyl-2-thioglycollic acid, 410.
1-(*o*-Carboxyphenyliminomethyl)*cyclo*hexan-2-one, 696.
Carcinogenics, hydrocarbon, colour test for, 584.
Castor oil, dihydroxystearic acid of, 387.

Cellulose, carbonisation of, 254.
Chloral, and its hydrate, **reaction of, with phenols, 718.**
Chloramine-*T*, reaction of, with arsine, hydrogen sulphide, and phosphine, 157.
Chloroamines, spectra of, absorption, 148.
Chromium hydroxide, sols, 293.
Cinchoninanilide, and 6-chloro-, 431.
Cinchoninic acid, 6-chloro-, and its derivatives, 428.
Cinchoninodiethylamide, 431.
Cinchoninomethylamide, 431.
Cinnolines, 353.
Coal, carbonisation of, 256.
Coke, petroleum, carbonisation of, 255.
Constitution, and antiplasmodial action, 401, 426.
Copper, reaction of, with iodine in aqueous potassium iodide, 598.
***p*-Cresol**, reaction of, with chloral, and its hydrate, 718.
Crotonic acid series, 220.

D.

Decalin-1:5-diol, 692.
Decalin-1:5-dione, and its diphenylhydrazone, 691.
Dehydrodeoxoglycyrrhetic acid, and its methyl ester, 539.
Dehydrodihydroelliptones, 592.
Dehydro-2-hydroxy-2-methylpyrrolizidine, and its picrolonate, 426.
Dehydro-oleanolic acid, 539.
Dehydrotetrahydroelliptone, 592.
and its *O*-acetyl derivative, 594.
Dehydrotetrahydromalaccol, and its *O*-diacetyl derivative, 595.
β-Deoxosiaresinonic acid, and its methyl ester, 543.
Deoxybenzoin, 4:4′-***di*cyano-, 115.
Deoxydeoxoglycyrrhetic acid, and its methyl ester, 538.
***iso*Derritol** methyl ether, 597.
***n*-** and ***iso*-Derritol *iso*flavones**, 597.
Desyl phenyl sulphide and thiobenzoate, 93, 94.
Desylthiol, 93.
β-Desylthiopropionic acid, 94.
Deuterium, determination of, in organic compounds, 370.
symmetrically placed, molecular dissymmetry due to, 370.
2:3-Dialkylquinolines, 693.
Diamidines, aromatic, trypanocidal activity of, 103.
4:4′-Diamidinoazobenzene *di*hydrochloride, 111.
4:4′-Diamidinobenzanilide, 111.
4:4′-Diamidinobenzenesulphonanilide *di*hydrochloride, 111.
4:4′-Diamidinobenzhydrol *di*hydrochloride, 110.
4:4′-Diamidinobenzophenone *di*hydrochloride, 110.
4:4′-Diamidino-*N*-benzoyldiphenylamine, 111.
4:4′-Diamidinobenzylideneacetophenone *di*hydrochloride, 110.
1:4-Di-(4′-amidinobenzyloxy)benzene *di*hydrochloride, 111.
4:4′-Diamidinodeoxybenzoin *di*hydrochloride, 110.
4:4′-Diamidinodibenzyl ether, and its dihydrochloride, 110.
4:4′-Diamidino-αδ-diphenoxybutane *di*hydrochloride, 110.
4:4′-Diamidinodiphenoxydimethyl ether, and its dihydrochloride, 111.
4:4′-Diamidino-αβ-diphenoxyethane *di*hydrochloride, 110.
4:4′-Diamidino-αη-diphenoxyheptane, and its hydrochloride, 110.
4:4′-Diamidino-αζ-diphenoxyhexane *di*hydrochloride, 110.
4:4′-Diamidinodiphenoxymethane *di*hydrochloride, 110.
Diamidino-αε-diphenoxypentanes, derivatives of, 110.
3:3′-Diamidino-αγ-diphenoxypropane *di*hydrochloride, 110.
4:4′-Diamidinodiphenyl sulphide, 110.
***di*sulphide *di*hydrochloride**, 111.
4:4′-Diamidinodiphenylamine, derivatives of, 116.
salts, 111.
4:4′-Diamidino-αδ-diphenylbutadiene *di*hydrochloride, 110.
4:4′-Diamidinodiphenylpropane *di*hydrochloride, 110.
4:4′-Diamidinodiphenylsulphone *di*hydrochloride, 110.
4:4′-Diamidinodiphenylurea *di*methanesulphonate, 111.
4:4′-Diamidinomethyldiphenyl *di*hydrochloride, 110.
ωω′-Di-(4′-amidinophenoxy)xylene *di*hydrochloride, 110.
4:4′-Diamidinostilbene, derivatives of, 110.
4:4′-Diamidinotriphenylmethane, *di*hydrochloride, 110.
Diastereoisomerides, separation of, by selective adsorption, 611.
Diazo-compounds, aromatic, decomposition reactions of, 266.
ω-Diazo-4-(4′-acetoxyphenoxy)acetophenone, 349.
Diazonium compounds, zinc chloride salts, decomposition of, by acetic anhydride, 747.
by alcohols and phenol, 581.
Di-α-benzoylbenzhydryl *di*sulphide, 94.
Dibenzoyltetraphenyltetrazan, equilibrium of, with **β**-benzoyl-αα-diphenylhydrazyl, 621.
Dibenzthioindigos, 413.
Dibenzthioindirubins, 413.
Dibenzyl, 3:3′-*di*hydroxy-, 687.
Dibenzyl ether, 4:4′-***di*amino-**, and **-*di*cyano-**, 114.
1:4-Dibenzyloxybenzene, 1:4-***di*-4′-cyano-**, 114.
3:4-Di-*tert.*-butylacenaphthene, and its picrate, 564.
3:4-Di-*tert.*-butylacenaphthenequinone, and its derivatives, 564.
4:5-Di-*tert.*-butylnaphthalic acid, derivatives of, 564.
3′:4′-Di-*tert.*-butyl-1:7′-thionaphthenacenaphthenylindigo, 565.
Di-*n*-decylacetophenone, 493.
Didesyl sulphide, 93.
Dienes, bimolecular, syntheses of, 612.
synthesis of, catalysis of, 618.
catalytic and solvent effects in, 625.
6:6-Diethoxyhex-4-yn-3-ol, and its urethane, 736.
2:5-Diethoxylaurophenone, and its 2:4-dinitrophenylhydrazone, 660.
2:5-Diethoxylaurylbenzene, 660.
6:6-Diethoxy-3-methylhex-4-yn-3-ol, and its urethane, 736.
2:5-Diethoxymyristophenone, and its 2:4-dinitrophenylhydrazone, 660.
2:5-Diethoxymyristylbenzene, 660.
2:5-Diethoxypalmitophenone 2:4-dinitrophenylhydrazone, 660.
2:5-Diethoxypalmitylbenzene, 660.
5:5-Diethoxy-1-phenyl-2-methylpent-3-yn-2-ol, and its urethane, 736.
2:5-Diethoxystearylbenzene, 660.
6:6′-Diethoxythioindigo, 412.
6:6′-Diethoxythioindirubin, 412.
4:4′-Di-*N*-ethylamidinodiphenyl *di*hydrochloride, 110.
Diethyl-δ-aminoamylamine, 6-chlorocinchoninamide of, 429.
α-Diethylamino-δ-amyl-*m*-aminobenzylamine, 427.
α-Diethylamino-δ-amylbenzylamine, 427.
α-Diethylamino-δ-amyl-6-chlorolepidylamine, 429.
α-Diethylamino-δ-amyl-lepidylamine, and its dipicrate, 427.
α-Diethylamino-δ-amyl-*p*-methoxybenzylamine, 427.
α-Diethylamino-δ-amyl-6-methoxylepidylamine, and its picrate, 428.
Diethylamino-ω-chlorohexane, 428.
2-(β-Diethylaminoethylamino)-4-methyl-7:8:2′:3′-pyridoquinoline, and its dihydrobromide, 218.
4-(β-Diethylaminoethylamino)-2-methyl-5:6:2′:3′-pyridoquinoline *di*picrate, 217.
4-(β-Diethylaminoethylamino)-2-methyl-7:8-2′:3′-pyridoquinoline, and its trihydrobromide, 217.
2-(β-Diethylaminoethylamino)-5:6:2′:3′-pyridoquinoline *di*picrate, 218.
6-Diethylaminohexanol, 428.
2-(δ-Diethylamino-α-methylbutylamino)-4-methyl-7:8:2′:3′-pyridoquinoline, and its picrate, 218.
4-(δ-Diethylamino-α-methylbutylamino)-2-methyl-5:6:2′:3′-pyridoquinoline *di*picrate, 217.
4-(δ-Diethylamino-α-methylbutylamino)-2-methyl-7:8:2′:3′-pyridoquinoline, and its tripicrate, 217.
2-(δ-Diethylamino-α-methylbutylamino)-5:6:2′:3′-pyridoquinoline, *di*picrate, 218.
3:5-Diethyl-4:6-dimethoxytoluquinone, 578.
Diflavylen, reaction of, with sulphur, 272.
Dihydrobetulanic acid, and its methyl ester, 41.
N^4-Dihydrochaulmoogrylsulphanilamide, 243.
Dihydrodeoxyelliptones, 591.
***l*-Dihydrodeoxy*iso*rotenone**, 593.
Dihydroderritol *iso*flavone, 597.
Dihydro-α-elemanic acid, 549.
Dihydro-β-elemanic acid, and its methyl ester, 550.
Dihydro-α-elemonic acid, and its methyl ester and oxime, 549.
Dihydro-β-elemonic acid, and its methyl ester, 550.
Dihydroelliptic acid, and its ethyl and methyl esters, 592.
Dihydroelliptol, 592.
Dihydroelliptones, and their derivatives, 591.
Dihydrofarnesene, and its derivatives, 119.
Dihydroindeno-2″:3″:2′:1′-benzanthrone, 627.
Dihydrojasmone, spectra of, absorption, and of its semicarbazone, 486.
Dihydromyrcene, preparation of, and its oxidation, 145.
Dihydromyrcene, ***mono-* and *di*-hydroxy-**, 148.
Dihydronerolidol, 119.

Dihydronorsiaresinol, 544.
9:10-Dihydrophenanthrene, 2:7-*di*hydroxy-, and its dibenzoyl derivative, 687.
9:10-Dihydrophenanthrene-3:3-dicarboxylic acid, 2:7-*di*hydroxy-, 687.
Dihydrorobustic acid, and its methyl ester, 182.
Dihydrosolasodine, 9.
Dihydrosqualene, *di*hydroxy-, 121.
Dihydrosulphanilylchaulmoogramide, 241.
2:2'-Diketodi*cyclo*pentyl, and its derivatives, 691.
3:10-Diketo-3:4:9:10:11:12-hexahydro-1:2-benzanthracene, 586.
4:4'-Dimethoxy-1:1'-azonaphthalene, 47.
2:6-Dimethoxybenzoquinone, alkenyl and alkyl derivatives, synthesis and anti-bacterial properties of, 577.
3:3'-Dimethoxydibenzyl, and 6:6'-*di*iodo-, 686.
2:7-Dimethoxy-9:10-dihydrophenanthrene, 686.
2:7-Dimethoxy-1:8-dimethylphenanthrene, 684.
2:5-Dimethoxylaurophenone, 660.
2:5-Dimethoxylaurylbenzene, 660.
2:5-Dimethoxy-1-methylnaphthalene, 690.
2:5-Dimethoxymyristophenone, 660.
2:5-Dimethoxymyristylbenzene, 660.
1:5-Dimethoxynaphthalene, bromination of, 236.
1:5-Dimethoxynaphthalene, 2:4-, 2:6-, 2:8-, and 4:8-*di*bromo-, 237.
2:5-Dimethoxypalmitophenone, 660.
2:5-Dimethoxypalmitylbenzene, 660.
1-2':5'-Dimethoxyphenylhexadecane, 1-hydroxy-, 661.
1-2':5'-Dimethoxyphenyl-Δ^1-hexadecene, 661.
1-2':5'-Dimethoxyphenyl-1-methyl-Δ^1-hexadecene, 661.
1-2':5'-Dimethoxyphenyl-1-methyl-Δ^1-octadecene, 661.
1-2':5'-Dimethoxyphenyl-1-methyl-Δ^1-tetradecene, 661.
$\alpha\beta$-Dimethoxypropionic acid, amide and methyl ester, 521.
2:5-Dimethoxystearophenone, 660.
2:5-Dimethoxystearylbenzene, 660.
4:6-Dimethoxytoluquinone, preparation of, 583.
$\alpha\gamma$-Dimethylallyl alcohol, esters, reactions of, 556.
4:4'-Dimethylamidinodiphenyl *di*hydrochloride, 110.
2:5-Dimethyl 3:6-anhydro-1-galactonamide, 231.
2:5-Dimethyl 3:6-anhydro-*l*-galactonic acid, 753.
Dimethylaniline, reaction of, with nitric acid, 584.
Dimethylaniline, *p*-amino-, derivatives of, 755.
2-chloro-4-amino-, and its derivatives, 2-chloro-4:6-*di*amino-, and its 4-acetyl derivative, 2:6-*di*chloro-4-amino-, 4-acetyl derivative, 2-chloro-4-nitro-, and 4-nitro-2-amino-, and its derivatives, 756, 757.
2:3-Dimethyl-5:6-benzoquinoline, and its picrate, 695.
4:6-Dimethylbenztriazole, and its hydrate, 422.
3:5-Dimethyl-4:6-dimethoxytoluquinone, 578.
3:3'-Dimethyldiphenyl-4:4'-bis-[2''-azo-8''-amino-1''-hydroxy-3'':6''-disulphonaphthalene-7''-(azo-2''':6'''-di-iodobenzene-4'''-arsonic acid)], *octa*sodium salt, 715.
3:3'-Dimethyldiphenyl-4:4'-bis-[2''-azo-8''-amino-1''-hydroxy-3'':6''-disulphonaphthalene-7''-(5'''-iodo-*o*-azotoluene)], and its tetrasodium salt, 715.
4:4'-Dimethyl-$\alpha\gamma$-diphenylpropane, 4:4'-*di*chloro-, and -dihydroxy-, 112.
2:2-Dimethylheptamide, 496.
1:2-Dimethyl*cyclo*hexane 3-hydro*per*oxide, 137.
1:2-Dimethyl*cyclo*hexane-1:2:3-triol, 137.
1:2-Dimethyl*cyclo*hexen-3-ol, and its α-naphthylurethane, 137.
3:7-Dimethylindole, 682.
2:2-Dimethyl-lauric acid, 492.
Dimethylnonylamine, and its methiodide, 403.
2:4-Dimethylpentenals, and their derivatives, 732.
1:1-Dimethyl-Δ^2-*cyclo*pentene-3:5-dicarboxylic acid, 208.
3:5-Dimethylphenoxyacetic acid, 2:4-*di*chloro-, 678.
4:7-Dimethyl-2-*iso*propyl-5-hydrindanone, 561.
4:7-Dimethyl-2-*iso*propyl-5-indanol, and its 3:5-dinitrobenzoate, 561.
2-(1:3-Dimethylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine, and its methosulphate, 712.
2-(1:3-Dimethylquinoxaline)-2-(1-methylbenzoxazole)trimethincyanine, and its iodide, 713.
2-(1:3-Dimethylquinoxaline)-2-(1:3:3-trimethylindoline)trimethincyanine, 712.
Dimethylselenetine bromide, 572.
2:2-Dimethylstearic acid, 492.
3:3-Dimethyltetradecoic acid, 494.
6:9-Dimethyl-1:2:3:4-tetrahydroacridine, and its picrate, 695.
2:4-Dimethylthiazole hydrochloride, 386.
4:4'-Dimethylthioindigo, 5:6'-*di*chloro-, 412.
7:7'-Dimethylthioindigo, 5:5'-*di*chloro-, 412.
4-$\alpha\alpha$-Dimethylundecylveratrole, 493.
$\alpha\delta$-Diphenoxybutane, 4:4'-*di*cyano-, 114.
$\alpha\kappa$-Diphenoxydecane, 4:4'-*di*cyano-, 114.
$\alpha\beta$-Diphenoxyethane, 4:4'-*di*cyano-, 114.
$\alpha\eta$-Diphenoxyheptane, 4:4'-*di*cyano-, 114.
$\alpha\zeta$-Diphenoxyhexane, 4:4'-*di*cyano-, 114.
Diphenoxymethane, 4:4'-*di*cyano-, 114.
$\alpha\epsilon$-Diphenoxypentane, 4:4'-*di*cyano-, 114.
$\alpha\gamma$-Diphenoxypropane, 4:4'-*di*cyano-, 114.
$\omega\omega'$-Diphenoxy-*p*-xylene, $\omega\omega'$-*di*-4'-cyano-, 114.
Diphenyl, 4-chloro-4'-hydroxy-, 4'-acetyl derivative, 583.
Diphenyl ether, 4-*mono*- and 4:4'-*di*-cyano-, 113.
hydroxy-carbonyl derivatives of, 347.
sulphide, 4:4'-*di*cyano-, 113.
4:4'-Di-*N*-phenylamidinodiphenyl *di*hydrochloride, 110.
Diphenylamine, 2-chloro-2'-nitro-, 505.
4:4'-*di*cyano-, *N*-benzoyl derivative, 116.
Diphenylamine-2-carboxylic acid, chloronitro-derivatives, 379.
Diphenylamine-4-carboxylic acid, 2-bromo-6-amino-, and -6-nitro-, and their derivatives, 505.
6-nitro-2-amino-, 502.
$\alpha\delta$-Diphenylbutadiene, 4:4'-*di*cyano-, 112.
$\alpha\delta$-Diphenylbutadiene-α-carboxylic acid, 4:4'-*di*nitro-, 112.
Diphenylchloroarsinealuminium, *tri*chloro-, 669.
***s*-Diphenyl-*p*-chlorophenylguanidine** hydrochloride, 152.
***NN*-Diphenyl-6-chloro-4-quinolylamidine**, 431.
Diphenyldi-*p*-tolylarsonium iodide, 669.
$\alpha\alpha$-Diphenylethylene, structure of, from dipole moments, 567.
$\alpha\alpha$-Diphenylethylene, 5-chloro-2-amino-4'-hydroxy-, and its dibenzoyl derivative, 357.
mono- and *di*-halogeno-derivatives, 568.
Diphenylmethane, *pp'*-*di*fluoro-, 568.
3:3'-*di*iodo-4:4'-*di*amino-, 715.
Diphenylmethane-4:4'-bis-(2''-azo-7''-amino-1''-hydroxy-3'':6''-disulphonaphthalene-8''-azobenzene-4'''-arsonic acid), 3:3'-*di*iodo-, *octa*potassium salt, 715.
Diphenylmethane-2:4'-dicarboxylic acid, 210.
$\alpha\gamma$-Diphenylpropane, 4:4'-*di*cyano-, 112.
1-(Diphenylyl-4'-iminomethyl)*cyclo*hexan-2-one, 695.
Diphenylsulphone, 4:4'-*di*amino-, carboxylic acids from, 42.
4:4'-*di*cyano-, 113.
Diphenylsulphone-4:4'-bisazo-β-naphthol, 243.
Diphenylsulphone-4:4'-bisazosalicylic acid, 244.
Dipole moments, measurement of, solvent effect in, 358, 497.
Di-*n*-propyl selenide *di*bromide, 572.
mercurichloride, 574.
2:2'-Dipyridyl sulphide *di*hydrobromide, 243.
2:2'-Dipyridylsulphone, 243.
Disulphanilylethyleneguanidine, 241.
2:2'-Disulphodiphenyl-4:4'-bis-[2''-azo-8''-amino-1''-hydroxy-3'':6''-disulphonaphthalene-7''-(azo-2'''-4'''-*di*iodobenzene-6'''-carboxylic acid)], 5:5'-*di*iodo-, *tri*sodium salt, 716.
2:2'-Disulphodiphenyl-4:4'-bis-[2''-azo-8''-amino-1''-hydroxy-3'':6''-disulphonaphthalene-7''-(azo-2''':6'''-*di*iodobenzene-4'''-sulphonic acid)], 5:5'-*di*iodo-, *octa*sodium salt, 716.
Dithioflavylen, reaction of, with sulphur, 272.
Dithioxanthylen, reaction of, with sulphur, 272.

E.

Earths, rare, mercury alloys with, 398, 523.
***n*- and *iso*-α-Elemanic acids**, and their methyl esters, 549.
β-Elemanic acids, and their methyl esters, 550.
Elliptic acid, and its ethyl and methyl esters, 592.
Elliptol, and its methyl ether, 592.
Elliptol *iso*flavone, 597.
Elliptone, reduction of, 587.
Elliptonone, 593.
Equilibrium, association, solvent effects in, 621.
Erucic acid, preparation and oxidation of, 477.
Ethaneselenonic acid, potassium salt, 572.
Ethers, aromatic, *di*- and *poly*-substituted, activation energies of, 676.
Ethinylcarbinols, preparation of, from $\alpha\beta$-unsaturated aldehydes, 733.
1-Ethinylgeraniol, and its acetyl derivative, 733.

Ethoxides, formation of, in ethyl alcohol, 526.
6′-Ethoxybenzthioindigos, 413.
Ethoxybenzthioindirubins, 412, 413.
5-Ethoxy-3′:4′-di-*tert.*-butyl-1:7′-thionaphthenacenaphthenylindigo, 565.
6-Ethoxylepidine, 2-amino-, 383.
***N*⁴-(6′-Ethoxy-2′-lepidyl)sulphanilamide**, 758.
2-Ethoxy-5-methyl-5-ethyl-Δ^2-dihydrofuran, 737.
6-Ethoxy-4′-methylthioindigo, 6′-chloro-, 412.
6′-Ethoxy-7-methylthioindigo, 5-chloro-, 412.
6′-Ethoxy-4-methylthioindirubin, 6-chloro-, 412.
6′-Ethoxy-7-methylthioindirubin, 5-chloro-, 412.
***N*⁴-(Ethoxy-4′-quinaldyl)sulphanilamides**, 758.
6-Ethoxythioindigo, 411.
6-Ethoxythioindirubin, 411.
3-(6-Ethoxythionaphthen)indole-indigo, 414.
6-Ethoxythionaphthenquinone-2-*p*-hydroxyanil, 410.
6-Ethoxythio-oxindole-3-aldehyde, 414.
3-Ethylaminomethylpyridine, and its salts, 432.
[2-(3-Ethylbenzoxazole)][3-(4-ethyl-2:4-benzthiazine)]trimethincyanine iodide, 102.
[2-(3-Ethylbenzthiazole)][3-(4-ethyl-2:4-benzthiazine)]-γ-azatrimethincyanine iodide, 102.
[2-(3-Ethylbenzthiazole)][3-(4-ethyl-2:4-benzthiazine)]trimethincyanine iodide, 102.
***o*-Ethylbenzyl** bromide, *o*-β-bromo-, and its use in syntheses, 737, 739.
ethyl ether, *o*-β-hydroxy-, 739.
3-Ethyl-*p*-cresol, 3-βββ-*tri*chloro-α-hydroxy-, and its derivatives, 719.
3-Ethyl-4:6-dimethoxytoluquinone, 578.
Ethylene linkings, cleavage of, by sulphur, 272.
by thionyl chloride, 725.
Ethylhexylamine, and its hydrochloride, 403.
Ethylhexylaminomethyl-6-methoxy-4-quinolylcarbinol and its dipicrate, 404.
Ethylnonylamine, and its hydrochloride, 403.
4-Ethyloct-4-en-1-yn-3-ol, preparation of, and its α-naphthylmethane, 735.
Ethyl-*n*-propylcarbinol, derivatives of, 25.
preparation of, and its phenylurethane, 734.
Eucarvone, spectra of, absorption, and of its derivatives, 483.
thiosemicarbazone, 486.

F.

Fehling's solution, titration of, with phenylhydrazine, 528.
Ferric hydroxide. See under Iron.
Films, surface, on solids, and on water, 696.
Fish, plants poisonous to, 181, 587, 593, 595.
Fluorine, 441.
Formo-4:4′-*di*bromobenzhydrylamide, 372.
Formo-4:4′-*di*bromo-2:3:5:6-tetradeuterobenzhydrylamide, 372.
2-Formylbenzoic acid, 3:5-*di*hydroxy-, and its methyl ester, and their 2:4-dinitrophenylhydrazones, 369.
Fucostadienone, and its derivatives, 392.
Fumaric acid, *trans-trans*-methyl ester, crystal structure of, 417.
Furan compounds, reactions of, 506.
Furanoisoflavones, synthesis of, 595.
Furfural, condensation of, with aniline and its hydrochloride, 506.

G.

Gadolinium, separation of, from neodymium, and samarium, 523.
Gas analysis, 26.
Gattermann reaction, 269.
Gelatin, amino-acids of, 337.
Glycine, carbonisation of, 255.
Glycyrrhetic acid, structure of, and its derivatives, 741.
in relation to oleanolic acid, 535.
Glyoxalines, preparation of, and their reactions with 2:4-dinitrochlorobenzene and picryl chloride, 383.

H.

Hashish, Egyptian, essential oil from, 188.
Hedraganic acid, preparation and structure of, 41.
Hemp, American. See Marihuana.
Hepta-acetyl *dl*-galactose, isolation of, from 3:6-anhydro-β-methyl-*d*-galactoside, 749.
***p*-*n*-Heptylbenzoic acid**, 308.
3-*n*-Heptylindole, 682.
***p*-*n*-Heptylphenyl methyl ketone**, and its derivatives, 308.
Heterocyclic compounds, syntheses of, 693.
3:4:7:8:9:10-Hexahydronaphtha(1:2:5:6)-bis-(2:3)-indole, 693.
Hexahydrosolasodiene, 10.
***cyclo*Hexane-1:1-diacetomethylimide**, 495.
***cyclo*Hexene** hydro*per*oxide, 132.
$\Delta^{2'}$-*cyclo*Hexenyl-Δ^2-*cyclo*hexene, *tetra*bromide, 518.
***n*-Hexoic acid**, βε-*di*bromo-, 424.
***p*-*n*-Hexylbenzoic acid**, 308.
3-*cyclo*Hexyl-7-methylindole, 682.
***p*-*n*-Hexylphenyl methyl ketone**, and its derivatives, 308.
Hormones, cortical, syntheses of substitutes for, 347.
Hugo Müller lecture, 79.
Hydrazoic acid. See Azoimide.
Hydrogen atoms, associating effect of, 420, 638.
symmetrically placed, molecular dissymmetry due to, 370.
Hydrogen sulphide, reaction of, with chloramine-*T*, 157.
Hypophosphites. See under Phosphorus.

I.

4-4″-Iminazolyldiphenyl ether, 2:4′-*di*hydroxy-, picrate, 350.
Indeno-2″:3″:2′:1′-benzanthrone, 626.
Indoles, 3-substituted, preparation of, 680.
Iodine, reaction of, with copper in aqueous potassium iodide, 598.
Periodic acid, reaction of, with polysaccharides, 183.
Ionisation in non-aqueous solvents, 526.
α- and β-**Ionones**, glycide acid and esters from, 732.
Iron:—
Ferric hydroxide, sols, 295.
Irone, spectrum of, absorption, 95.
thiosemicarbazones, spectra of, absorption, 483.
Isethionic acid, and its salts, 716.

K.

Keratin, wool, amino-acids of, 338.
5-Keto-6-acetyl-6-carbethoxy-3:3-dimethylundecoic acid, ethyl ester, 493.
Ketobehenic acid, hydroxy-, and its semicarbazone, 481.
9′-Keto-3′(or 4′)-*tert.*-butyl-8′-azaphenalino-(7′:8′:2:3)-ψ-indole, 564.
1-γ-Ketobutyl-2-keto-1:2:3:4-tetrahydronaphthalene, 1-hydroxy-, 688.
1-γ-Ketobutyl-2-naphthol, reduction of, 684.
9′-Keto-3′:4′-di-*tert.*-butyl-8′-azaphenalino(7′:8′:2:3)-ψ-indole, 564.
3-Keto-4:5-dihydrodi(1:2)pyrrole, and its derivatives, 425.
21-Ketodihydro-oleananic acid, methyl ester, 543.
2-Keto-1:3-dimethyl-3:5-di-*n*-decyl-2:3-dihydropyrroie, 495.
5-Keto-3:3-dimethyl-lauric acid, and its 2:4-dinitrophenylhydrazone, 495.
β-Keto-αγ-di-(1-methyl-2-pyrrolidyl)butyric acid, ethyl ester, *di*picrate, 424.
5-Keto-3:3-dimethylundecoic acid, and its 2:4-dinitrophenylhydrazone, 494.
1-Keto-3-*cyclo*hexenyl-Δ^2-octahydrophenanthrene, and their derivatives, 395.
1″-Ketoindeno-2″:3″:2′:1′-benzanthrone, 628.
2-Keto-5-β-*p*-methoxyphenylethyltetrahydrofuran, 35.
2-Keto-5-*p*-methoxystyryl-2:3-dihydrofuran, and its dibenzoyl derivative, 35.
5-Keto-3-methyl-3-*n*-amyldecoic acid, ethyl ester, 496.
5-Keto-3-methyl-3-*n*-decylpentadecoic acid, ethyl ester, 496.
5-Keto-3-methyl-3-*n*-hexylnonoic acid, 494.
5-Keto-3-methyl-3-*n*-octyl-lauric acid, methyl ester, 495.
5-Keto-3-methyl-3-*n*-octylundecoic acid, 494.
Ketones, aromatic, condensation of, with ethyl succinate, 585.

1-β-Ketononyl*cyclo*hexane-1-acetic acid, 495.
2-Keto-5-β-phenylethyltetrahydrofuran, 34.
4-Keto-1-phenyl-1:2:3:4-tetrahydro-2-phenanthroic acid, 587.
2′-Ketopiperazino(6′:4′:1:9)carbazole, 505.
2-Ketopyrrolizidine, and its picrolonate, 426.
Ketostearic acids, hydroxy-, oxidation of, in presence of alcoholic alkali, 204.
2-Keto-5-styryl-2:3-dihydrofuran, and its derivatives, 34.

L.

Laminarin, end-group assay of, 578.
Lanthanum hydroxide, sols, 297.
Laurylbenzoquinone, 661.
Laurylquinol, 660.
Lectures delivered before the Chemical Society, 70, 79, 337, 441, 448, 457, 467.
Lepidines, 2-chloro-, reaction of, with ammonia, 381.
Lepidylamine, derivatives of, 426.
N^1-Lepidylsulphanilamide, 428.
N^1-Lepidylsulphanilamide, 6-chloro-, 429.
N^4-(2′-Lepidyl)sulphanilamide, 758.
Lignan group, chemistry of, 448.
Linkings, co-valent, fission of, 153.
double, additions to, 612.

M.

Malonyl *mono*chloride, preparation of, 45.
***d*- and *l*-Mandelic acid**, *l*-menthyl esters, adsorption of, on alumina, 611.
Manganous salts, reaction of, with sodium silicate in solution, 581.
Maniladiol, constitution of, 198.
Maniladione, and its derivatives, 203.
Marihuana, resin from, 628.
Memorial Lecture, Sir J. J. Thomson, 467.
Mercury alloys with rare-earth metals, 398, 523.
Metallic hydroxides, sols, equilibria and ageing in, 277.
Methaneselenonic acid, potassium salt, 572.
Methoxides, formation of, in methyl alcohol, 526.
10-Methoxyacridone, 8-chloro-2-nitro-, 381.
α-Methoxyacrylic acid, derivatives of, 520, 522.
***p*-Methoxybenzhydrol**, derivatives of, 605.
***p*-Methoxybenzhydryl ether**, 609.
methyl ether, 609.
4′-Methoxybenzophenone, 5-chloro-2-amino-, 356.
1-Methoxybenzthiazole, isomerisation of, 307.
7-Methoxy-9:10-dihydrophenanthrene, 2-hydroxy-, 687.
7-Methoxy-9:10-dihydrophenanthrene-3-carboxylic acid, 2-hydroxy-, 687.
5-Methoxy-1:1-dimethyl-β-tetralone, and its derivatives, 691.
6-Methoxylepidine, 2-amino-, 383.
N^1-(6-Methoxylepidyl)sulphanilamide, 428.
N^4-(6′-Methoxy-2′-lepidyl)sulphanilamide, 758.
3-Methoxy-4-(4′-methoxyphenoxy)benzoic acid, 350.
2′-Methoxy-5′-methylbenzophenone, 5-chloro-2-amino-, and its *N*-acetyl derivative, 357.
5-Methoxy-1-methyl-β-tetralone, and its semicarbazone, 690.
1-Methoxynaphthalene, 2:4-*di*bromo-5-hydroxy-, 5-acetyl derivative, 237.
5-Methoxynaphthalene, 2:8-*di*bromo-1-hydroxy-, 1-acetyl derivative, 238.
5-Methoxy-1:4-naphthaquinone, 2-*mono*- and 2:6- and 2:8-*di*bromo-, 238.
5-Methoxy-1-naphthol, bromination of, 236.
5-Methoxy-1-naphthol, 2-*mono*- and 2:6-, 2:8-, and 6:8-, *di*bromo-, 237.
7-Methoxyphenanthrene, 2-hydroxy-, 686.
4-(4′-Methoxyphenoxy)acetophenone, and its 2:4-dinitrophenylhydrazone, 351.
4-(4′-Methoxyphenoxy)benzaldehyde semicarbazone, 353.
4-(4′-Methoxyphenoxy)benzoic acid, 349.
4-(4′-Methoxyphenoxy)cinnamic acid, and its methyl ester, 352.
β-4-(4′-Methoxyphenoxy)phenylpropionic acid, methyl ester, 352.
4-*m*-Methoxyphenylacetylresorcinol, 688.
1-(Methoxyphenyliminomethyl)*cyclo*hexan-2-ones, 696.
β-*o*-Methoxyphenylpropaldehyde, and its *p*-nitrophenylhydrazone, 182.
2-Methoxyphenyltrimethylammonium hydroxide, 4-nitro-, salts of, 271.
6-Methoxyphthalanil, 5-*mono*- and 3:5-*di*-bromo-, 239.
6-Methoxyphthalic anhydride, 5-*mono*- and 3:5-*di*-bromo-, 238.
α-Methoxypropionic acid, β-*mono*- and αβ-*di*-bromo-, β-chloro-, and β-hydroxy-, derivatives of, 521.
β-Methoxypropionic acid, α-bromo-, amide, and α-chloro-, amide and methyl ester, 521.
6- and 8-Methoxyquinaldines, 4-amino-, 382.
N^4-(Methoxy-4′-quinaldyl)sulphanilamides, 758.
6-Methoxyquinoline, carbinolamines from, 401.
5-Methoxy-2-tetradecylcoumaran, 661.
Methoxy-1:2:3:4-tetrahydroacridines, and their picrates, 696.
7-Methoxy-1:2:3:4-tetrahydrophenanthrene, 2-hydroxy-, 687.
5-Methoxy-β-tetralone, 690.
Methyl ethyl and *n*-propyl selenide mercurichlorides, 573.
***d*-5′-Methyl-7-*n*-amyl-3:4-*cyclo*hexenocoumarin**, *d*-5-hydroxy-, and its acetate, 187.
Methyl-*n*-amylsulphone, 54.
Methylaniline, 2-chloro-6-*mono*- and -6-*N*-*di*-nitro-4-amino-, 2-chloro-6-nitro-*N*-nitroso-4-amino-, and *N*-nitroso-4-amino-, 4-acetyl derivatives, 756, 757.
2-Methylanilinovinylbenzoxazole ethiodide, 712.
2-Methylanilinovinylbenzthiazole methiodide, 712.
2-Methylanilinovinylquinoline methiodide, 712.
Methylation, biological, 574.
2′-Methyl-1′-aza-3:4-benzpyrene, 4′-chloro-, and 4′-hydroxy-, 377.
5′-Methylbenzophenone, 5-chloro-2-amino-2′-hydroxy-, and its dibenzoyl derivative, and 2:5-*di*chloro-2′-hydroxy-, 357.
4′-Methylbenzthioindigos, 6′-chloro-, 412.
7′-Methylbenzthioindigos, 5′-chloro-, 412.
7-Methyl-5′:6′-benzthioindirubin, 5-chloro-, 413.
7′-Methyl-6:7-benzthioindirubin, 5′-chloro-, 412.
5-Methyl-2-butyl-5-*n*-amyl*cyclo*hexane-1:3-dione, 496.
Methyl-*n*-butylcarbinol, derivatives of, 25.
Methyl-*n*-butylsulphone, 54.
3-Methyl-2-decylcoumaran, 5-hydroxy-, 661.
β-Methyl-β-*n*-decylglutarimide, αα′-*di*cyano-, 495.
2-Methyl-2-*n*-decyl-lauronitrile, 493.
α-Methyl-α-*n*-decylsuccinic acid, anhydride and imide, 495.
Methyldinonylamine, 403.
5:5′-Methylenebis-2-hydroxy-3:4-dimethoxybenzoic acid, 727.
6:6′-Methylenebis-4-hydroxy-3:5-dimethoxyphthalide, 727.
Methylenebis-*p*-toluenesulphonmethylamide, 30.
6:6′-Methylenebis-3:4:5-trimethoxyphthalide, 726.
5(4)-3′:4′-Methylenedioxystyrylglyoxaline, 4(5)-nitro-, 233.
Methyleneimines, cyclic, 29.
(+)- and (−)-γ-Methyl-α-ethylallyl alcohols, reactions of, and its derivatives, 18.
2-(3-Methyl-1-ethylquinoxaline)-1-(4-dimethylaminobenzene)-dimethincyanine, and its ethosulphate, 712.
Methyl-*d*-galactonic acid, pentamethyl ester, 753.
5(4)-Methylglyoxaline, 4(5)-nitro-, methosulphate, 235.
1-Methylglyoxaline-4-carboxylic acid, 5-nitro-, and its amide, 235.
1-Methylglyoxaline-5-carboxylic acid, 4-nitro-, and its methyl ester, 235.
1-Methyl-1-heptyloctan-1-ol, 493.
3-Methyl-2-hexadecylcoumaran, 5-hydroxy-, 661.
4-Methylhex-2-enal, 4-hydroxy-, semicarbazone, 737.
1-Methyl*cyclo*hexene hydro*per*oxide, 136.
1-Methyl*cyclo*hexenol, 136.
4-Methylhex-4-en-1-yn-3-ol, and its α-naphthylurethane, 735.
2-Methyl-2-(β-*cyclo*hexylethyl)lauric acid, ethyl ester, 496.
3-Methyl-3-(β-*cyclo*hexylethyl)nonoic acid, ethyl ester, 495.
β-Methyl-β-*n*-hexylglutaric acid, 494.
6-Methyl-4-hydroxy-3:5-dimethoxyphthalide, 6-chloro-, 727.
***N*-Methyl-lepidylamine**, and its dihydrochloride, 431.
1-Methyl-2-methylenebenzthiazoline-ω-aldehyde, 712.
Methyl γ-methyl-α-ethylallyl ether, 26.
Methylnonylamine, and its hydrochloride, 403.
Methylnonylaminomethyl-6-methoxy-4-quinolylcarbinol, and its dipicrate, 404.
5-Methyl-2-*n*-nonyl-5-*n*-decyl*cyclo*hexane-1:3-dione, 496.
1-Methyl-1-*n*-octyldecoic acid, 493.
β-Methyl-β-*n*-octylglutarimide, and αα′-*di*cyano-, 494.

N-Methyl*iso*oxazolidine methiodide and methopicrate, 433.
β-Methylpentane-ββε-tricarboxylic acid, and its quinine salt, and γ-hydroxy-, lactone, 208.
β-Methylpentane-ββεε-tetracarboxylic acid, ethyl ester, 208.
N-Methyl-*m*-phenanthrolinium methyl sulphate, 217.
5′-Methylphenylcinnoline, 6-chloro-4-2′-hydroxy-, and its benzoate, 358.
Methyl β-phenylethyl ketone *di*nitrophenylhydrazone, 62.
β-Methyl*iso*propyl alcohol, αβ-*di*chloro-, 171.
Methylpyridoquinolines, chloro-, and hydroxy-, 215, 216.
4-Methylpyrrole-2-acetic acid, 3-hydroxy-, ethyl ester, and its *p*-nitrobenzoyl derivative, 426.
1-Methylpyrrolidine-2-acetic acid, ethyl ester, synthesis of, 422.
2-Methylpyrrolizidine, and its picrate, and 2-hydroxy-, and its picrolonate, 426.
synthesis of, 424.
2-Methylquinoline, 5-amino-4-hydroxy-, and its acetyl derivative, 215.
4-Methylquinoline, 6-chloro-4-amino-, and its dihydrochloride, 429.
Methylselenium *tri*bromide, 572.
3-Methylsorbic aldehyde, 2:4-*di*nitrophenylhydrazone, 737.
3-Methyl-2-tetradecylcoumaran, 5-hydroxy-, 661.
7-Methyl-1:2:3:4-tetrahydroacridine, and its picrate, 695.
8-Methyl-1:2:3:4-tetrahydroacridine, and its picrate, 695.
9-Methyl-1:2:3:4-tetrahydroacridine, and its picrate, 695.
N-Methyltetrahydro*iso*oxazine, salts, 433.
1-Methyl-β-tetralone, and its semicarbazone, 690.
5-Methylthiazole, and its salts, 386.
4-Methylthioindigo, 6-chloro-, 411.
7-Methylthioindigo, 5-chloro-, 412.
4-Methylthioindirubin, 6-chloro-, 411.
Methylthionaphthenindole-indigos, chloro-, 414.
Methylthio-oxindole-3-aldehydes, chloro-, and their derivatives, 414.
6-Methyl-3:4:5-trimethoxyphthalide, 6-chloro-, 726.
β-Methyltrimethylene-αγ-bis-2-naphthyl ether, β-hydroxy-, 171.
N-Methyltrimethylenemine methiodide, 174.
Molecular compounds. See Organic compounds, molecular.
Moulds, metabolic products of, synthesis of compounds related to, 368.
Mucilage, seed, 58.
Muconic acid, *trans-trans*-methyl ester, crystal structure of, 417.
Myosin, rabbit, amino-acids of, 339.
Myristylbenzoquinone, 661.
Myristylquinol, 660.

N.

Naphthalene, 2:4- and 2:6-*di*bromo-1:5-*di*hydroxy-, 237.
2-bromo-5-nitro-, 2-chloro-5-nitro-, 2:4-*di*chloro-5-nitro-, 2-iodo-5-nitro-, and 1:2-*di*iodo-5-nitro-, 724.
1:5-*di*hydroxy-, and its diacetyl derivative, bromination of, 236.
2-nitro-, preparation of, 744.
Naphthalenes, nitro-, reactions of, 45.
Naphthalenediazonium sulphates, nitro-, decomposition of, by cuprous hydroxide, 744.
α- and β-Naphthalenesulphinic acids, copper and nickel salts, 263.
Naphthalides, halogenation and nitration of, 723.
1:4-Naphthaquinone, 2-bromo-5-hydroxy-, 5-acetyl derivative, and 2:6-*di*bromo-5-hydroxy-, 238.
Naphtha(1′2′:4:5)thiazole, 2:4′-*di*chloro-, 375.
α- and β-Naphthoic acids, copper and nickel salts of, 263.
1-Naphthol, 2:4-*di*bromo-5-hydroxy-, 5-acetyl derivative, 237.
1-Naphthyl ethers, 4-nitro-, exchange reactions of, with sodium alkoxides, 45.
1-Naphthylamine, 2-bromo-5-nitro-, 2:4-*di*bromo-5-nitro-, 2:4-*di*chloro-5-nitro-, 2-iodo-5-nitro-, 5-nitro-, 2-mercuriacetate, and 2:4:5-*tri*nitro-, 724.
5-nitro-, halogenation and nitration of, 723.
3-(α- and β-Naphthyliminomethyl)butan-2-ones, 695.
1-(α- and β-Naphthyliminomethyl)*cyclo*hexan-2-ones, 695.
α-Naphthylthiocarbimide, and 4-chloro-, 374.
1-Naphthylthioglycollic acid, 2-amino-, acetyl derivative, and 2-chloro-, 415.
Neodymium, separation of, from gadolinium and samarium, 523.
Neodymium hydroxide, sols, 300.
Nicotine, azeotrope of, with water, 511.
Nicotinethylamide, 432.
Nitric acid, reaction of, with dimethylaniline, 584.
Nonaldehyde, peroxide from, 218.
Norechinocystadienol, and its acetate, 539.
Norsiaresinodione, 543.
Norsiaresinone, 543.

O.

Obituary Notices :—
Alfred Clay Abraham, 475.
Lancelot Salisbury Bagster, 333.
Thomas Bennett Case, 333.
Robert John Flintoff, 64.
Herbert Freundlich, 646.
Arthur Geake, 475.
Andrew McKeown, 476.
William Macnab, 64.
William Lash Miller, 334.
Hermann Günther Gottschalt Mohrhenn, 67.
William Reginald Ormandy, 68.
James Alexander Pond, 476.
Robert Robison, 69.
Leonard Temple Thorne, 336.
Henry Harben Whitelegg, 71.
Octahydrodeoxyelliptone, 591.
n-Octane-αδεθ-tetracarboxylic acid, 518.
ethyl ester, 692.
p-*n*-Octylphenyl methyl ketone, and its derivatives, 308.
2-*n*-Octylundecamide, 493.
Oleadienols I and II, 539.
Oleadienone II, 539.
Oleanolic acid, structure of, and its derivatives, 741.
Olefine *per*oxides, structure and reactivity of, 121.
Organic compounds, determination in, of deuterium, 370.
molecular, formation and structure of, 245.
Ovomucoid, carbohydrate residue in, 550.
*iso*Oxazolidine, 432.
salts, 433.
Oxidobrassidic acid, methyl ester, 482.
Oxidoerucic acid, methyl ester, 482.
d-Oxidostearic acid, 390.
Oxyacid radicals, exchange of heavy oxygen between water and, 631.
Oxygen, heavy isotope, exchange of, between inorganic oxyanions and water, 631.

P.

Palmitic acid, 4-methoxyphenyl ester, 660.
Palmitylbenzoquinone, 661.
Palmitylquinol, 660.
Pectic substances, chemistry of, 70.
Pedler lecture, 457.
Penicillium, action of, on aliphatic seleninates and selenonates, 574.
Pentadeuteropyrocatechol, 396.
*cyclo*Pentadiene, compound of, with benzoquinone, 623.
syntheses with, catalysis of, 618.
Pentaerythritol, amino-derivatives, 163, 175.
Pentane-αβ-dicarboxylic acid, ε-bromo-, 423.
Pentaphenylguanidine hydrochloride, 152.
Perhydro-2-methyl-5:6-benzochroman, 688.
Periodic acid. See under Iodine.
2-Phenacyl-2-methyl-lauric acid, 496.
2-Phenacyl-2-methyloctoic acid, 496.
Phenanthrene, 2:7-*di*hydroxy-, *di*benzoate, 686.
preparation of, 684.
m-Phenanthroline, derivatives of, 213.
Phenazine, 1-nitro-, 502.
Phenol, *m*-chloro-, coupling of, with diazotised aniline, 434.
3-chloro-2:4- and -4:6-*di*amino-, dibenzoyl derivatives, 435.
Phenols, methylation of, nuclear, 682.
reaction of, with chloral and its hydrate, 718.
Phenols, *m*-halogeno-, coupling of, with diazotised aniline, 433.

Phenol ethers, halogenation of, 418, 676.
4-Phenoxyacetophenone, 4-4′-hydroxy-, and its derivatives, 351.
3:4-4′-*di*hydroxy-, and its 2:4-dinitrophenylhydrazone, 351.
ω:4-4′-*di*hydroxy-, and its diacetyl derivative, 350.
ω:3:4-4′-*tri*hydroxy-, triacetyl derivative, 350.
Phenoxybenzenedisulphonamide, *p*-nitro-, 242.
4-Phenoxybenzenesulphonamide, 4-*p*-nitro-, 242.
4-Phenoxybenzoic acid, 4-4′-hydroxy-, and its derivatives, 349.
3:4-4′-*di*hydroxy-, and its derivatives, 350.
γ-Phenoxybutaldehyde, and its semicarbazone, 424.
2-Phenoxy-6-ethoxylepidine, 383.
4-Phenoxy-6- and **-8-ethoxyquinaldines,** 383.
β-Phenoxyethyl bromide, β-4-cyano-, 114.
β-Phenoxyethylaniline, 4:4′-*di*cyano-, 114.
ε-Phenoxy-Δ^{α}-hexenoic acid, 424.
2-Phenoxylepidine, 383.
5-Phenoxy-2-methoxybenzoic acid, and its ethyl ester, 352.
2-Phenoxy-6-methoxylepidine, 383.
4-Phenoxy-6- and **-8-methoxyquinaldines,** 383.
ε-Phenoxypentane-αβ-dicarboxylic acid, and its imide, and *di*bromo-, 423.
ε-Phenoxypentane-αββ-tricarboxylic acid, and its triethyl ester, 423.
β-4-Phenoxyphenylpropionic acid, β-4-4′-hydroxy-, and its ethyl ester, 352.
4-Phenoxyquinaldine, 383.
4-Phenoxyquinoline, and its salts, 383.
Phenyl α-benzoylbenzhydryl sulphide, 95.
carbonate, parachor and structure of, 661.
βββ-*tri*chloro-α-hydroxyethyl ether, 719.
4-cyanobenzyl ether, 3- and 4-cyano-, 113.
*iso*cyano*di*chloride, *p*-chloro-, 152.
4-cyano-β-phenylethyl ether, 4-cyano-, 116.
αγ-dimethylallyl ether, 558.
nitro-β-phenylethyl ether, 2-nitro-4-cyano-, 115.
β-phenylethyl ether, 4-cyano-, 115.
Phenylacetamidine, 4-amino-, *di*hydrochloride, 110.
5-Phenylacetylbenzoic acid, 2:4-*di*hydroxy-, methyl ester, 687.
O-Phenylacetylisethionic acid, sodium salt, 717.
4-Phenylacetylsalicylic acid, 2-hydroxy-, methyl ester, 687.
3-Phenylacridine, and its picrate, 695.
1-(*p*-Phenylaminophenyliminomethyl)*cyclo*hexan-2-one, 696.
7-Phenylamino-1:2:3:4-tetrahydroacridine, and its picrate, 696.
***C*-Phenylanthranil,** 4-nitro-*C*-*p*-chloro-, 380.
1′-Phenylbenzanthrone-2′-carboxylic acid, and its ethyl ester, 628.
***N*-Phenylbenziminochloride,** *N*-4-cyano-, 116.
***N*-Phenylbenzimino-4′-cyanophenyl ether,** *N*-4-cyano-, 116.
1-Phenylbenztriazole-5-carboxylic acid, 7-bromo-, 505.
γ-Phenyl-γ-benzylmethylsuccinic acid, 586.
Phenyl-(5-bromo-2-aminophenyl)methylcarbinol, and its derivatives, 355.
α-Phenyl-α-(5-bromo-2-benzamidophenyl)ethylene, 355.
α-Phenylbutyric acid, α-bromo-, 223.
α-Phenylbutyryl bromide, α-bromo-, 222.
α-Phenylbutyrylcarbamide, α-bromo-, 223.
***N*-Phenyl-6-chlorolepidylamine,** and its derivatives, 431.
4-Phenylcinnoline, 6-bromo-, 355.
6-chloro-4-4′-hydroxy-, and its benzoate, 357.
α-Phenylcrotonic acid, amide and chloride of, 222.
α-Phenylcrotonylcarbamide, 222.
***N*-Phenyl-1:4-** and **-1:5-dimethylglyoxalinium chlorides,** *N*-2:4-dinitro-, 386.
1-Phenyl-2:3-dimethyl-5-pyrazolone-*x*-sulphonic acid, and its derivatives, 243.
o-Phenylenediamine, condensation of, with ethyl acetoacetate, 303.
Phenylethinylcarbinol, preparation of, and its derivatives, 734.
β-Phenylethyl bromide, 4-amino-, hydrochloride, and 4-cyano-, 115.
5-Phenylethylbenzoic acid, 2:4-*di*hydroxy-, methyl ester, 688.
Phenylhydrazine, oxidation of, by cupric salts, potentiometry of, 528.
α-Phenyl-α-(2′-hydroxy-5′-methylphenyl)ethylene, α-5-chloro-2-amino-, and its derivatives, 357.
Phenylimidocarbonic acid, and *p*-bromo-, and *p*-nitro-, esters, 153.
1-(Phenyliminomethyl)*cyclo*hexan-2-one, bromo-, chloro-, hydroxy-, iodo-, and nitro-derivatives, 695.
1-(Phenyliminomethyl)-4-methyl*cyclo*hexan-2-one, 695.
***N*-Phenyl-lepidylamine,** 431.
γ-Phenyl-α-methyl-α-*n*-decylbutyrolactones, 496.
2-(1-Phenyl-3-methylquinoxaline)-1-(4-dimethylaminobenzene) dimethincyanine, and its chloride, 713.
2-(1-Phenyl-3-methylquinoxaline)-2-(1:3:3-trimethylindoline)-trimethincyanine, and its acetate, 713.
γ-Phenyl-γ-naphthylitaconic acid, and its derivatives, 586.
γ-Phenyl-γ-naphthylmethylsuccinic acid, 587.
***O*-β-Phenylpropionylisethionic acid,** sodium salt, 717.
3-γ-Phenylpropylindole, 682.
2-(1-Phenylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine, and its iodide, 713.
2-(1-Phenylquinoxaline)-2-(1:3:3-trimethylindoline)trimethincyanine, and its iodide, 713.
7-Phenyl-1:2:3:4-tetrahydroacridine, and its picrate, 695.
γ-Phenyl-γ-(6-tetralyl)itaconic acid, 587.
Phenyltrimethylammonium hydroxide, nitro-, salts of, 271.
Phenyltri-*p*-tolylarsonium salts, 669.
Phenylurethane, *p*-nitro-, 152.
Phosphorus *tri*hydride, reaction of, with chloramine-*T*, 157.
*penta*chloride, crystal structure of, 642.
Hypophosphites, determination of, with potassium permanganate, 307.
Phosphorylase, potato, starch synthesis by, 55.
Phthalic acid, 3:5-*di*hydroxy-, synthesis of, 370.
4′-Phthalimidodiphenylsulphone, 4-amino-, 44.
Phytosterols, oxidation of, with Oppenhauer reagent, 391.
***N*-Picryl-1:4-dimethylglyoxalinium chloride,** 386.
Picryl-2-methylthiazole, 385.
***N*-Picryl-2-methylthiazolium chloride,** 385.
Picrylthiazole, 385.
Plants, leguminous, fish-poison, active principles of, 181, 587, 593, 595.
Plant gums, chemistry of, 70.
Plantago arenaria, mucilage from seeds of, 58.
Poisons, plant, for fish, 181, 587, 593, 595.
Polyene series, 727, 733, 735.
Polyisoprenes, 116, 513.
autoxidation in, 121, 139.
Polysaccharides, end-group assay of, 578.
Polysaccharides, reaction of, with periodic acid, 183.
Porcupine quill, *X*-ray structure of, 345.
Potassium dichromate, standardisation of sodium thiosulphate, 366.
Propane-1-selenonic acid, potassium salt, 573.
Propargyl acetal, carbinols from, 735.
3-Propenyl-4:6-dimethoxytoluquinone, 578.
Propenylethylcarbinol, preparation of, and its derivatives, 734.
3-*n*-Propyl-4:6-dimethoxytoluquinone, 578.
2′-*iso*Propyldiphenyl-2-carboxylic acid, 2′-α-hydroxy-, and its brucine salt, 437.
***n*-Propylhexylamine,** and its hydrochloride, 403.
Propylhexylaminomethyl-6-methoxy-4-quinolylcarbinol, and its dipicrate, 404.
3-Propylindoles, 681.
Propylnonylamine, and its hydrochloride, 403.
Proteins, stoicheiometry of, and *X*-rays, 337.
Pulegone, condensation products of, with olivetol and orcinol, 185.
Purine nucleosides, constitution of, 232.
β-3-Pyrenylaminocrotonic acid, ethyl ester, 377.
Pyrethrins I and II, structure of, and their absorption spectra, 671.
Pyridine, 2-amino-, sodium *N*-methylenebisulphite, 244.
2-thiol-, derivatives of, 584.
Pyridoquinolines, chloro-, and hydroxy-, 216.
5:6:2′:3′-Pyridoquinolinium methyl sulphate, 217.
***N*-(3′-Pyridyl)anthranilic acid,** 726.
***N*-(4′-Pyridyl)anthranilic acid,** hydrochloride, 726.
2-Pyridyl*iso*thiourea, 2-5-amino-, and -5-nitro-, hydrochlorides, 584.
Pyrrolidine-2-acetic acid, ethyl ester, and its picrolonate, 426.
Pyrrolidine-1:2-diacetic acid, ethyl ester, 426.
2-(2′-Pyrrolidone-5′-carboxy-4″-aminobenzenesulphonamido) pyridine, 243.
2-Pyrrolidone-5-carboxyamino-3′-toluene-*x*-sulphonamide, 243.
2-Pyrrolidone-5-carboxy-α-naphthalides, 243.
2-Pyrrolidone-5-carboxy-*p*-nitroanilide, 243.
2-Pyrrolidone-5-carboxy-*m*-toluidide, 243.

Q.

Quinaldines, 4-chloro-, reaction of, with ammonia, 381.
N^4-(4′-Quinaldyl)sulphanilamide, 758.
Quininic acid, 403.
Quinoline, 8-hydroxy-, preparation of, 415.
Quinoline-4-aldehyde anil, 431.
Quinoline-4-carboxylic acid, 7-amino-2-hydroxy-, and its ethyl ester, 216.
Quinoline-2:4-dicarboxylic acid, 6-chloro-, 428.
8-Quinolyl *p*-nitrophenyl ether, 242.
N^4-Quinolylsulphanilamide, 243.
Quinoxaline cyanines, 710.

R.

Reactions, aromatic, side-chain, polar effect of substituents in, 191.
Report of the Council, 311.
Resins, American hemp, 628.
elemi Manila, acids of, 544.
diols of, 198.
Robustic acid, and its derivatives, 181.
Rubber, 116, 513.
caoutchol constituent of, 223.
hydrochloride, crystal structure of, 654.

S.

Samarium, separation of, from gadolinium and neodymium, 523.
Sandmeyer reaction, 266, 376, 720.
Sapogenins, 35, 532, 535, 540, 544, 741.
Scopulariopsis brevicaulis, action of, on aliphatic seleninates and selenonates, 574.
Seeds, mucilage of, 58.
Selenium organic compounds, 570.
Siaresinolic acid, 540.
α- and β-Siaresinonic acids, methyl esters, 543.
Sitostenone, derivatives of, 393.
Sodium silicate, reaction of, with manganous salts in solution, 581.
sulphite, reaction of, with betaine, 48.
thiosulphate, standardisation of, with potassium dichromate, 366.
Sodium organic compounds:—
Sodium ethoxide, exchange reaction of, with 4-nitro-1-naphthyl, methyl ether, 45.
methoxide, exchange reaction of, with 4-nitro-1-naphthyl ethyl ether, 45.
Solanum, alkaloids of, 1, 3, 12, 17.
Solanum auriculatum, alkaloids from, 12.
Solanum aviculare, fruit, alkaloid from, 1.
Solasodiene, 10.
Solasodine, and its derivatives, 8.
Solasonine, 2, 3.
Solauricidine, and its derivatives, 14.
Solauricine, 14, 17.
Solvents, non-aqueous, ionisation in, 526.
Sophochrysine, and its derivatives, 508.
Sophora alkaloids, 507, 555.
Sophora chrysophylla, alkaloids of, 507.
Squalene *hexa*hydrochlorides, synthesis of, 120.
Stains, vital, 713.
Starch, constitution of, synthesised by potato phosphorylase, 55.
Stearic acid, 4-methoxyphenyl ester, 660.
Stearic acid, 9:10-*di*hydroxy-, from castor oil, 389.
Stearylbenzene, 2:4:5-*tri*hydroxy-, triacetyl derivative, 661.
Stearylbenzoquinone, 661.
Stearylquinol, 660.
Stereochemistry, basis of, 457.
Sterols, synthesis of substances related to, 684.
Sterol group, 391.
Stigmastadienone, derivatives of, 393.
Stilbene, 3:4′-*di*amino-, *mono*-, and *di*-cyano-, 4-nitro-4′-amino-, and its acetyl derivative, and 4-nitro-4′-cyano-, 111, 112.
Styrylethinylcarbinol, 735.
4-Styryl-1-methylglyoxaline, 5-nitro-, 235.
5-Styryl-1-methylglyoxaline, 4-nitro-, 235.
Succinic acid, ethyl ester, condensation of, with aromatic ketones, 585.
Sulphanilamide, bactericidal derivatives of, 239.
benzoyl derivatives, 241.
quinoline derivatives, 758.
Sulphanilyladipamide, 241.
Sulphanilylaminoethylpyridinium bromide, 242.
Sulphanilylchaulmoogramide, 241.
Sulphanilylglutamic acid, and its sodium salt, 242.
Sulphanilylmyristamide, 241.
***di*Sulphides,** organic, reactions of, with betaine, 48.
2-(4′-Sulphobenzeneazo)-1-amino-8-naphthol-3:6-disulphonic acid, 2-2′:6′-*di*iodo-, trisodium salt, 716.
Sulphur, fission by, of ethylene linkings, 272.
Sulphur–hydrogen–nitrogen linkings, 638.
Sulphur organic compounds, 90.

T.

Terpenoid compounds, spectra of, absorption, 95, 483, 486.
Tetra-arylarsonium salts, 666.
Tetra-arylphosphonium salts, 666.
Tetra-arylstibonium salts, 666.
2:3:5:6-Tetradeuterobenzhydrylamine, 4:4′-*di*bromo-, and its attempted resolution, 370.
2:3:5:6-Tetradeuterobenzophenone, 4:4′-*di*bromo-, 372.
1:2:3:4-Tetrahydroacridine, amino-, bromo-, chloro-, hydroxy-, iodo-, and nitro-derivatives, and their derivatives, 695.
6:7:8:9-Tetrahydro-1:2-benzacridine, and its picrate, 695.
***d*-Tetrahydrocannabinol,** synthesis of, 185.
***dl*-Tetrahydrocannabinol** *l*-menthoxyacetate, 188.
Tetrahydroelliptic acid, and its methyl ester, 594.
and its methyl ester methyl ether, 593.
Tetrahydroelliptol, 593.
(—)-Tetrahydrofurfuryl alcohol, rotatory dispersion of, 531.
Tetrahydromalaccolic acid, and its methyl ester, 594.
Tetrahydro*iso*oxazine, salts and derivatives of, 433.
Tetrahydro-1:2-*iso*oxazine, 432.
Tetrahydropyrethrin II, 676.
Tetrahydropyrethrolone, spectra of, absorption, and of its semicarbazone, 486.
1:2:3:4-Tetrahydro*iso*quinoline, derivatives of, 737.
***p*-(2-1:2:3:4-Tetrahydro*iso*quinolyl)benzenesulphonic acid,** and its amide, 740.
2-(*p*-(2′-1′:2′:3′:4′-Tetrahydro*iso*quinolyl)benzenesulphonyl)-1:2:3:4-tetrahydro*iso*quinoline, 739.
Tetrakisdimethylaminomethylmethane *tetra*hydrochloride, thermal decomposition of, 163.
quaternary salts, formation and decomposition of, 175.
Tetrakismethylaminomethylmethane, and its derivatives, 167.
*tetra*hydrochloride, thermal decomposition of, 163.
β-Tetralone, preparation of, from β-naphthol, 689.
Tetramethyl *l*-galactose anilide, 754.
***d*-2:2:5′:4″-Tetramethyl-3′:4′:5′:6′-tetrahydrodibenzopyran,** *d*-6″-hydroxy-, 187.
Tetraphenylarsonium salts, 669.
1:2:4:5-Tetraphenylbenzene, preparation of, from benzylideneacetophenone, 585.
αα′α″α‴-Tetraphenyl-γγ′-dithiopyrylen, and **ββ′-*di*chloro-,** 274.
αγδζ-Tetraphenyl-$d^{\alpha\epsilon}$-hexadiene, αζ-*di*chloro-, 585.
Tetraphenylphosphonium thiocyanate, 670.
***s*-Tetraphenyltolylguanidines,** 152.
Tetratolylarsonium salts, 670.
Tetratolylphosphonium iodides, 670.
Thiazinocyanines, 98.
Thiazole hydrochloride, 385.
Thiazoles, preparation of, and their reactions with 2:4-dinitrochlorobenzene and picryl chloride, 383.
***p*-Thioacetamidoazobenzene,** 641.
***p*-Thioacetamidobenzoic acid,** ethyl ester, 641.
2-Thioacetamido-5:4′-dimethylazobenzene, 641.
Thioacetanthranilic acid, methyl ester, 641.
Thioacetbenzylanilide, 641.
Thioacetethylanilide, 641.
Thioacetnitroanilides, 641.
Thioacet-*m*-toluidide, 641.
Thioamides, association in, 638.

Thiobenzobenzylanilide, 641.
Thiobenzoic acid, α-benzoylbenzhydryl ester, 94.
Thiocarbimides, aromatic, action of chlorine on, 150.
Thioethers, constitution of, and their sensitivity to alkali, 90.
Thioindigoid dyes, constitution of, 404.
Thiols, constitution of, and their sensitivity to alkali, 90.
Thionaphthenquinones, reactivity of carbonyl groups in, 404.
Thionyl chloride, cleavage of ethylene linkings by, 725.
Thiopropion-*p*-toluidide, 641.
Thomson Memorial Lecture, 467.
Thorium hydroxide, sols, 300.
Tilden lectures, 70, 441, 448.
2-o-Toluenesazo-1-amino-8-naphthol-3:6-disulphonic acid, 2-5′-iodo-, *di*sodium salt, 714.
***p*-Toluenesulphinic acid**, copper and nickel salts, 263.
1-*p*-Toluenesulphonamido-2:5-dimethylpyrrole, 726.
***p*-Toluenesulphonic acid**, copper and nickel salts, 265.
***p*-Toluenesulphon-1-naphthalide**, 5-*mono*-, and 2:4:5-*tri*-nitro-, 724.
9-*p*-Toluenesulphonylcarbazole, and 1-amino-, 3-bromo-, 1-nitro-, and 3:7-*di*nitro-, and their derivatives, 510.
9-Toluenesulphonylcarbazoles, nitro-, 503, 504.
***p*-Toluidinoaceto-*p*-toluidide**, *N*-nitroso-, 54.
***p*-Tolyl ββ*β*-*tri*chloro-α-hydroxyethyl ether**, 719.
4-cyanobenzyl ether, ω-cyano-, 113.
***p*-Tolyl-α-anisylethylsulphone**, 610.
***p*-Tolylbenzhydrylsulphone**, 610.
***o*-Tolylimidocarbonic acid**, *p*-tolyl ester, 153.
***p*-Tolylimidocarbonic acid**, phenyl ester, 153.
1-(Tolyliminomethyl)*cyclo*hexan-2-ones, 695.
***p*-Tolyl-*p*-methoxybenzhydrylsulphone**, 610.
***o*-Tolyltrimethylammonium** hydroxide, 4-nitro-, salts of, 272.
***p*-Tolylurethane**, 152.
Transport numbers, measurement of, solute concentration adjustment in, 678.
Trimethin[2-(3-ethyldihydro-6:7-benzbenzoxazole)][3-(2:4-benzthiazine)], 101.
Trimethin[2-(3-ethyldihydro-4:5-benzbenzthiazole)][3-(2:4-benzthiazine)], 102.
Trimethin[2-(3-ethyldihydrobenzoxazole)][3-(2:4-benzthiazine)], 101.
Trimethin[2-(3-ethyldihydrobenzselenazole)][3-(2:4-benzthiazine)], 102.
Trimethin[2-(3-ethyldihydrobenzthiazole)][3-(2:4-benzthiazine)], 101.
3:4:5-Trimethoxybenzoic acid, phthalides from, 726.
2:5:3′-Trimethoxydibenzyl, 687.
2:4:5-Trimethoxylaurophenone, 660.
1-2′:4′:5′-Trimethoxyphenyl-1-methyl-Δ^1-duodecene, 661.
3:4:5-Trimethoxyphthalidylglyoxylic acid, ethyl ester, 727.
Trimethyleneimine hydriodide, 174.
1:3:3-Trimethyl-Δ^1-*cyclo*hexene-4-carboxylic acid, 206.
8-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-3:6-dimethylocta-4:6-dien-3-ol, 733.
3-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-1-methylcrotonaldehyde, and its use in vitamin-*A* syntheses, 727.
7-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-5-methylhepta-3:5-dien-2-one, and its semicarbazone, 733.
6-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-4-methylhex-4-en-1-yn-2-ol, and its acetyl derivative, 733.
3:4:6-Trimethyl β-methylglucoside, 2-amino-, acetyl derivative, 553.
2′:2′:6′-Trimethylpiperidinomethyl-6-methoxy-4-quinolylcarbinol, and its dipicrate, 404.
***NN′N″*-Trimethyltrimethylenetriamine**, action of benzene- and toluene-sulphonyl chlorides on, 30.
Triphenylarsinealuminium, *tri*chloro-, 669.
Triphenylmethane, 4:4′-*di*cyano-, 111.
α-Triphenylmethylthioacetic acid, α-*p*-nitro-, 92.
Triphenyl-*p*-tolylarsonium salts, 669.
Tris(phenyl*di*chloroarsine)aluminium, *tri*chloro-, 670.
Triterpene acids, structure of, 35, 532.
Triterpene group, 198.
Tri-o-tolylarsine, hydroxyoxy- and oxy-halides of, 670.

U.

4(5)-Ureidoglyoxaline-5(4)-carboxylic acid, and its methyl ester, and salts, 234.
Ursanic acid, and its methyl ester, 41.
Ursolic acid, preparation and structure of, 41.

V.

Vetivazulene, synthesis of, 559.
Vinylethinylcarbinol, preparation of, and its derivatives, 735.
Vitamin-*A*, synthesis of, 727.
Volume, molecular, structure and, 661.
Vulcanisation, mechanism of, 513.

X.

Xanthine, synthesis of, 232.
Xylene, autoxidation of alkyl groups in, 185.
1-(*p*-Xylyliminomethyl)*cyclo*hexan-2-one, 695.

Y.

Yeast-adenylic acid, synthesis of, 231.
Yeast-ribonucleic acid, constitution of, 231.

Z.

Zinc chloride, double salts of diazonium compounds with, decomposition of, 581, 747.

FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order, C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

CH_3Br_2Se Methylselenium tribromide, 572.
CH_4O_3Se Methaneselenonic acid, potassium salt, 572.

C_2 Group.

C_2HOCl_3 Chloral, reaction of, with phenols, 718.
$C_2HO_2Cl_3$ Trichloroacetic acid, mercurous and quinol salts, electric polarisation of, 565.
$C_2H_5O_2N$ Glycine, carbonisation of, 255.
$C_2H_6O_3Se$ Ethaneseloninic acid, potassium salt, 573.
$C_2H_4O_4S$ Isethionic acid, and its salts, 716.

C_3 Group.

C_3H_3NS Thiazole, hydrochloride of, 385.
C_3H_7ON *iso*Oxazolidine, and its salts, 433.
$C_3H_8O_3Se$ Propane-1-selenonic acid, potassium salt, 573.
C_3H_8NI Trimethyleneimine hydriodide, 174.

3 IV

$C_3H_8Cl_2HgSe$ Methyl ethyl selenide mercurichloride, 573.

C_4 Group.

C_4H_6 Butadiene, bimolecular dimerisation of, 612.

4 III

C_4H_5ON α-Methoxyacrylonitrile, 522.
C_4H_5NS Methylthiazoles, 385.
$C_4H_7O_2N$ α-Methoxyacrylamide, 522.
$C_4H_8OCl_2$ αγ-Dichloro-β-methyl*iso*propyl alcohol, 171.
C_4H_9ON Tetrahydro-1:2-*iso*oxazine, and its salts, 432.
$C_4H_9O_2N$ β-Hydroxy-α-methoxypropionamide, 521.

4 IV

C_4H_6ONBr β-Bromo-α-methoxypropionitrile, 522.
$C_4H_7O_2NBr_2$ αβ-Dibromo-α-methoxypropionamide, 522.
$C_4H_8O_2NCl$ Chloromethoxypropionamides, 521.
$C_4H_8O_2NBr$ Bromomethoxypropionamides, 522.
$C_4H_{10}Cl_2HgSe$ Methyl *n*-propyl selenide mercurichloride, 574.

C_5 Group.

C_5H_6 *cyclo*Pentadiene, catalytic syntheses with, 618.

5 II

$C_5H_{10}O_2$ Tetrahydrofurfuryl alcohols, rotatory dispersion of, 531.
$C_5H_{11}F$ *tert.*-Amyl fluoride, 499.
$C_5H_{14}N_2$ αγ-Bismethylaminopropane, and its salts, 168.
$C_5H_{16}N_4$ Tetrakisaminomethylmethane, 167.

5 III

$C_5H_4O_2N_4$ Xanthine, synthesis of, 232.
$C_5H_5O_4N_3$ 5-Nitro-1-methylglyoxaline-4-carboxylic acid, 235.
$C_5H_6O_3N_4$ 5-Nitro-1-methylglyoxaline-4-carboxyamide, 236.
4(5)-Ureidoglyoxaline-5(4)-carboxylic acid, 234.
C_5H_7NS 2:4-Dimethylthiazole, and its hydrochloride, 386.
$C_5H_9O_2Br$ Methyl β-bromo*iso*butyrate, 425.

$C_5H_9O_3Cl$ Methyl α-chloro-β-methoxypropionate, 521.
$C_5H_9O_3Br$ Methyl β-bromo-α-methoxypropionate, 522.
$C_5H_{11}O_2N$ Betaine, reactions of, with aromatic amines, organic sulphides, and sodium sulphite, 48.
$C_5H_{11}O_3N$ αβ-Dimethoxypropionamide, 521.
Methyl α-methoxyacrylamide, 522.
$C_5H_{12}O_2S$ Methyl-*n*-butylsulphone, 54.
$C_5H_{12}NI$ *N*-Methyltrimethyleneimine methiodide, 174.

5 IV

$C_5H_{12}ONI$ *N*-Methyl*iso*oxazolidine methiodide, 433.

C_6 Group.

C_6H_8O Propenylethinylcarbinol, 734.
$C_6H_6O_4$ *trans-trans*-Methyl fumarate, crystal structure of, 417.
$C_6H_8N_2$ *o*-Phenylenediamine, condensation of, with ethyl acetoacetate, 303.
Phenylhydrazine, oxidation of, by cupric salts, 528.
$C_6H_{10}O_2$ *cyclo*Hexene hydroperoxide, 132.
$C_6H_{10}O_3$ Ethyl acetoacetate, condensation of, with *o*-phenylenediamine, 303.
$C_6H_{10}O_4$ Ethyl succinate, condensation of, with aromatic ketones, 585.
$C_6H_{11}Cl$ *dl*-γ-Methyl-α-ethylallyl chloride, 25.
$C_6H_{12}O$ γ-Methyl-α-ethylallyl alcohols, reactions of, 18.
$C_6H_{12}O_4$ Methyl αβ-dimethoxypropionate, 521.
$C_6H_{15}N_3$ *NN'N''*-Trimethyltrimethylenetriamine, action of benzene- and toluene-sulphonyl chlorides on, 30.
$C_6O_2Br_4$ 2:3:5:6-Tetrabromobenzoquinone, preparation of, 583.

6 III

$C_6HO_2D_5$ Pentadeuteropyrocatechol, 396.
$C_6H_3O_2I$ 2-Iodobenzoquinone, preparation of, 375.
$C_6H_7O_4N_3$ Methyl 4-nitro-1-methylglyoxaline-5-carboxylate, 235.
$C_7H_8O_3N_4$ Methyl 4(5)-ureidoglyoxaline-5(4)-carboxylate, 234.
$C_6H_9N_4S$ 2-(5-Aminopyridyl)*iso*thiourea, dihydrochloride of, 584.
$C_6H_{10}O_2Br_2$ βε-Dibromo-*n*-hexoic acid, 424.
$C_6H_{11}O_3N$ Carbethoxy*iso*oxazolidine, 433.
$C_7H_{13}O_2N$ β-Carbethoxy-*n*-propylamine, and its picrate, 425.
$C_6H_{14}O_2S$ Methyl-*n*-amylsulphone, 54.
$C_6H_{14}Br_2Se$ Di-*n*-propyl selenide dibromide, 572.

6 IV

$C_6H_6O_3N_2S$ *p*-Nitrobenzenesulphenamide, 244.
$C_6H_7ON_2Cl$ 3-Chloro-2:4-diaminophenol, 435.
$C_6H_8O_3N_2S$ 5-Amino-2-hydroxybenzenesulphonamide, 709.
$C_6H_8O_2N_2S$ *p*-Aminobenzenesulphonhydrazide, 740.
$C_6H_{11}O_6N_3S$ 4(5)-Nitro-5(4)-methylglyoxaline methosulphate, 235.
$C_6H_{13}O_2BrSe$ Dimethylselenetine bromide, 572.
$C_6H_{14}ONI$ *N*-Methyltetrahydro*iso*oxazine, 433.
$C_6H_{14}Cl_2HgSe$ Di-*n*-propyl selenide mercurichloride, 574.

6 V

$C_6H_7O_3N_2SNa$ Sodium 2-aminopyridine-*N*-methylenebisulphite, 244.

C_7 Group.

C_7H_8O *p*-Cresol, reaction of, with chloral and its hydrate, 718.
$C_7H_8O_2$ Acetylvinylethinylcarbinol, 735.
$C_7H_{10}O$ *iso*Butenylethinylcarbinol, 735.
4-Methylhex-4-en-1-yn-3-ol, 735.
$C_7H_{12}O$ 2:4-Dimethylpent-2-enal, 732.
1-Methyl*cyclo*hexenol, 136.
$C_7H_{12}O_2$ 1-Methyl*cyclo*hexene hydroperoxide, 136.
$C_7H_{14}O$ Methyl γ-methyl-α-ethylallyl ether, 26.
$C_7H_{14}O_3$ 1-Methyl*cyclo*hexane-1:2:3-triol, 136.

7 III

$C_7H_6O_2S$ *p*-Thiolbenzoic acid, preparation and properties of, 376.
$C_7H_8O_2S$ *p*-Toluenesulphinic acid, copper and nickel salts, 264.
$C_7H_8O_3S$ *p*-Toluenesulphonic acid, copper and nickel salts, 264.
$C_7H_{11}ON$ 2-Ketopyrrolizidine, and its picrolonate, 426.
$C_7H_{11}O_4Br$ ε-Bromopentane-αβ-dicarboxylic acid, 423.
$C_7H_{13}O_3N$ *N*-Carbethoxytetrahydro*iso*oxazine, 433.
$C_7H_{18}ON_2$ αγ-Bisdimethylamino*iso*propyl alcohol, 172.

7 IV

$C_7H_7O_4NS$ Methyl *p*-nitrobenzenesulphinate, 244.

C_8 Group.

C_8H_{10} Xylene, autoxidation of alkyl groups in, 185.

8 II

$C_8H_6O_5$ 3:5-Dihydroxy-2-formylbenzoic acid, 369.
$C_8H_8O_4$ 4:6-Dimethoxytoluquinone, preparation of, 583.
$C_8H_9N_3$ 4:6-Dimethylbenztriazole, 422.
$C_8H_{10}O_2$ Acetylpropenylethinylcarbinol, 734.
$C_8H_{10}O_4$ *trans-trans*-Methyl muconate, crystal structure of, 417.
$C_8H_{11}N$ Dimethylaniline, reaction of, with nitric acid, 584.
$C_8H_{11}N_3$ 4-Aminophenylacetamidine, dihydrochloride of, 110.
$C_8H_{12}O$ Acetyl*cyclo*hexene, self-condensation of, 393.
$C_8H_{13}N_3$ 3-Ethylaminomethylpyridine, and its salts, 432.
$C_8H_{13}N$ Dehydro-2-hydroxy-2-methylpyrrolizidine, and its picrolonate, 426.
$C_8H_{14}O$ 1:2-Dimethyl*cyclo*hexen-3-ol, 137.
$C_8H_{14}O_3$ 1:2-Dimethyl*cyclo*hexane 3-hydroperoxide, 137.
dl-γ-Methyl-α-ethylallyl acetate, 25.
$C_8H_{14}O_6$ 2:5-Dimethyl 3:6-anhydro-*l*-galactonic acid, 753.
$C_8H_{15}N$ 2-Methylpyrrolizidine, and its picrate, 424.
$C_8H_{16}O_3$ 1:2-Dimethyl*cyclo*hexane-1:2:3-triol, 137.
$C_8H_{19}N$ Ethylhexylamine, and its hydrochloride, 403.
$C_8H_{20}N_2$ αγ-Bisdimethylamino-β-methylpropane, and its salts, 171.

8 III

C_8H_7ON 4-Cyanobenzyl alcohol, 114.
$C_8H_7O_2Cl_3$ Phenyl ββ*β*-trichloro-α-hydroxyethyl ether, 719.
$C_8H_9O_2N$ 4-Carbamidobenzyl alcohol, 114.
$C_8H_{10}ON_2$ Nicotinethylamide, 432.
$C_8H_{10}NBr$ 4-Amino-β-phenylethyl bromide, and its hydrochloride, 115.
$C_8H_{10}N_2Cl_2$ 2:6-Dichloro-4-aminodimethylaniline, 757.
$C_8H_{11}O_3N$ Ethyl 3-hydroxy-4-methylpyrrole-2-acetate, 426.
$C_8H_{11}N_2Cl$ 2-Chloro-4-aminodimethylaniline, and its stannichloride, 756.
$C_8H_{15}ON$ 2-Hydroxy-2-methylpyrrolizidine, and its picrolonate, 426.
$C_8H_{15}ON_3$ 2:4-Dimethylpent-2-enal semicarbazone, 732.
$C_8H_{15}O_2N$ Ethyl pyrrolidine-2-acetate, and its picrolonate, 426.
$C_8H_{15}O_2N_3$ 4-Hydroxy-4-methylhex-2-enal semicarbazone, 737.
$C_8H_{15}O_5N$ 2:5-Dimethyl 3:6-anhydro-*l*-galactonamide, 231.
$C_8H_{19}N_2Cl$ β-Chloro-αγ-bisdimethylamino-β-methylpropane, and its salts, 172.
$C_8H_{20}ON_2$ αγ-Bisdimethylamino-β-methyl*iso*propyl alcohol, and its salts, 171.

8 IV

C_8H_4ONCl 4-Cyanobenzoyl chloride, 115.
$C_8H_5O_5N_2Br$ 4-Bromo-3:5-dinitroacetophenone, 501.
$C_8H_8O_2N_2S$ Thioacetnitroanilides, 641.
$C_8H_9O_4NS$ Ethyl *p*-nitrobenzenesulphinate, 244.
$C_8H_{10}O_4N_2S$ 5-Acetamido-2-hydroxybenzenesulphonamide, 709.
$C_8H_{11}ONS$ 1-Methoxybenzthiazole, isomerisation of, 307.

C_9 Group.

$C_9H_8O_5$ Methyl 3:5-dihydroxy-2-formylbenzoate, 369.
$C_9H_{10}Br_2$ *o*-β-Bromoethylbenzyl bromide, preparation of, and its use in syntheses, 737.
$C_9H_{12}O_4$ 1:1-Dimethyl-Δ^2-*cyclo*pentene-3:5-dicarboxylic acid, 208.
$C_9H_{12}N_4$ 4-Amidinomethylbenzamidine, dihydrochloride of, 110.
$C_9H_{14}O_6$ β-Methylpentane-βδε-tricarboxylic acid, 208.
$C_9H_{16}O_2$ 2-Ethoxy-5-methyl-5-ethyl-Δ^3-dihydrofuran, 737.
$C_9H_{21}N$ *n*-Propylhexylamine, and its hydrochloride, 403.
$C_9H_{24}N_4$ Tetrakismethylaminomethylmethane, and its salts, 167.

9 III

$C_9H_4O_4Br_2$ 3:5-Dibromo-6-methoxyphthalic anhydride, 239.
$C_9H_5O_4Br$ 5-Bromo-6-methoxyphthalic anhydride, 238.
C_9H_8NBr 4-Cyano-β-phenylethyl bromide, 115.
$C_9H_9O_3Cl_3$ *p*-Tolyl ββ*β*-trichloro-α-hydroxyethyl ether, 719.
$C_9H_{10}O_4N_2$ *p*-Nitrophenylurethane, 152.
$C_9H_{11}OBr$ *o*-Bromobenzyl ethyl ether, 739.
$C_9H_{11}O_2N_3$ *N*-Nitroso-4-acetamidomethylaniline, 756.
$C_9H_{11}NS$ Thioacet-*m*-toluidide, 641.
$C_9H_{14}O_4N_2$ Nitrophenyltrimethylammonium hydroxide, salts, 271.
$C_9H_{17}O_2N$ Ethyl 1-methylpyrrolidine-2-acetate, synthesis of, 422.
$C_9H_{19}ON$ 2:2-Dimethylheptamide, 496.

9 IV

$C_9H_4O_6N_4S$ Picrylthiazole, 385.
C_9H_6ONBr β-4-Cyanophenoxyethyl bromide, 114.

$C_9H_9O_4NS$ α-(*p*-Nitrobenzylthio)acetic acid, 92.
$C_9H_9O_4N_4Cl$ 2-Chloro-6-nitro-*N*-nitroso-4-acetamidomethylaniline, 757.
$C_9H_9O_5N_4Cl$ 2-Chloro-6-*N*-dinitro-4-acetamidomethylaniline, 757.
$C_9H_{10}O_3N_2Cl$ 2-Chloro-6-nitro-4-acetamidomethylaniline, 757.
$C_9H_{11}O_2NS$ α-(*p*-Aminobenzylthio)acetic acid, 92.
$C_9H_{24}ON_2I_2$ αγ-Bisdimethylamino*iso*propyl dimethiodide, 172.

C_{10} Group.

$C_{10}H_{18}$ Dihydromyrene, preparation and oxidation of, 145.

10 II

$C_{10}H_{11}N$ 3:7-Dimethylindole, 682.
$C_{10}H_{12}O_4$ 3:5-Dimethyl-4:6-dimethoxytoluquinone, 578.
$C_{10}H_{12}O_4$ 3-Ethyl-4:6-dimethoxytoluquinone, 578.
$C_{10}H_{14}O_2$ Decalin-1:5-dione, 692.
2:2′-Diketodi*cyclo*pentyl, 691.
$C_{10}H_{14}N_2$ Nicotine, azeotrope of, with water, 511.
$C_{10}H_{16}O_2$ 1:3:3-Trimethyl-Δ^1-*cyclo*hexene-4-carboxylic acid, 206.
$C_{10}H_{18}O$ Bis-αγ-dimethylallyl ether, 559.
Hydroxydihydromyrcene, 148.
$C_{10}H_{18}O_2$ Decalin-1:5-diol, 692.
Dihydroxydihydromyrcene, 148.
$C_{10}H_{23}N$ *n*-Butylhexylamine, and its hydrochloride, 402.
Methylnonylamine, and its hydrochloride, 403.

10 III

$C_{10}H_5N_2Cl$ 6-Chlorocinchoninonitrile, 429.
$C_{10}H_6O_2Br_2$ Dibromo-1:5-dihydroxynaphthalenes, 237.
$C_{10}H_7O_2N$ 2-Nitronaphthalene, preparation of, 744.
$C_{10}H_8O_3S$ α- and β-Naphthalenesulphinic acids, copper and nickel salts, 265.
$C_{10}H_8O_2N_2$ 7-Amino-2-hydroxyquinoline-4-carboxylic acid, 216.
$C_{10}H_9OCl$ α-Phenylcrotonyl chloride, 222.
$C_{10}H_9O_5N_3$ 3:5-Dinitrobenz*iso*oxazolidide, 433.
$C_{10}H_9N_2Cl$ 6-Chloro-4-aminomethylquinoline, and its dihydrochloride, 429.
$C_{10}H_{10}ON_2$ 5-Amino-4-hydroxy-2-methylquinoline, 215.
Benziminazole-2-acetone, 304.
$C_{10}H_{10}OBr_2$ α-Bromo-α-phenylbutyryl bromide, 222.
$C_{10}H_{10}O_3Cl_2$ 2:4-Dichloro-3:5-dimethylphenoxyacetic acid, 678.
$C_{10}H_{10}O_4N_2$ Acetoacet-*o*-nitroanilide, 304.
$C_{10}H_{11}O_2Br$ α-(Bromophenyl)butyric acid, 223.
$C_{10}H_{12}O_5S$ *O*-Phenylacetylisethionic acid, sodium salt, 717.
$C_{10}H_{13}O_2N$ *p*-Tolylurethane, 152.
$C_{10}H_{13}O_3N_3$ 4-Nitro-2-acetamidodimethylaniline, 756.
$C_{10}H_{13}NS$ Thioacetethylanilide, 641.
Thiopropion-*p*-toluidide, 641.
$C_{10}H_{16}O_3N_2$ 4-Nitro-*o*-tolyltrimethylammonium hydroxide, salts, 272.
$C_{10}H_{16}O_4N_2$ 4-Nitro-2-methoxyphenyltrimethylammonium hydroxide, salts, 271.
$C_{10}H_{19}O_4N$ Carbethoxymethyl-β-carbethoxy-*n*-propylamine, and its picrolonate, 426.
$C_{10}H_{22}NCl$ Diethylamino-ω-chlorohexane, 428.
$C_{10}H_{23}ON$ 6-Diethylaminohexanol, 428.
$C_{10}H_{24}ON_2$ αγ-Bisdimethylamino-β-ethoxy-β-methylpropane, 172.
$C_{10}H_{24}N_2I_2$ αγ-Bistrimethylammonium-β-methylpropenylene di-iodide, 172.

10 IV

$C_{10}H_5O_2NCl_2$ 2:4-Dichloro-5-nitronaphthalene, 724.
$C_{10}H_5O_2NI_2$ 1:2-Di-iodo-5-nitronaphthalene, 724.
$C_{10}H_6O_2NCl$ 6-Chlorocinchoninic acid, 428.
2-Chloro-5-nitronaphthalene, 724.
$C_{10}H_6O_2NBr$ 2-Bromo-5-nitronaphthalene, 724.
$C_{10}H_6O_2N_2Cl_2$ 2:4-Dichloro-5-nitro-1-naphthylamine, 724.
$C_{10}H_6O_2N_2Br_2$ 2:4-Dibromo-5-nitro-1-naphthylamine, 724.
$C_{10}H_6O_6N_4S$ Picryl-2- and -5-methylthiazoles, 385.
$C_{10}H_7O_2ClS$ Chloromethylthio-oxindole-3-aldehydes, 414.
$C_{10}H_7O_2N_2Br$ 2-Bromo-5-nitro-1-naphthylamine, 724.
$C_{10}H_7O_2N_2I$ 2-Iodo-5-nitro-1-naphthylamine, 724.
$C_{10}H_8O_2N_2S$ 2:2′-Dipyridylsulphone, 243.
$C_{10}H_9ONS$ 1-Methyl-2-methylenebenzthiazoline-ω-aldehyde, 712.
$C_{10}H_{10}N_2Br_2S$ 2:2′-Dipyridyl sulphide dihydrobromide, 243.
$C_{10}H_{11}O_2NS$ Methyl thioacetanthranilate, 641.
$C_{10}H_{11}O_4NS$ β-(*p*-Nitrobenzylthio)propionic acid, 92.
$C_{10}H_{12}ON_2Cl_2$ 2:6-Dichloro-4-acetamidodimethylaniline, 757.
$C_{10}H_{12}O_3N_2Cl$ 2-Chloro-6-nitro-4-acetamidodimethylaniline, 757.
$C_{10}H_{12}ON_2Cl$ 2-Chloro-4-acetamidodimethylaniline, 756.
$C_{10}H_{13}N_2IS$ 3-Amino-2:4-benzthiazine ethiodide, 101.
$C_{10}H_{14}ON_2Cl$ 2-Chloro-6-amino-4-acetamidodimethylaniline, 757.
$C_{10}H_{14}O_7N_5P$ Yeast adenylic acid, synthesis of, 231.

10 V

$C_{10}H_7O_6N_4ClS$ *N*-Picryl-2-methylthiazolium chloride, 385.
$C_{10}H_{10}O_5NClS$ Acetamidoacetoxybenzenesulphonyl chlorides, 709.

C_{11} Group.

$C_{11}H_8O_2$ α- and β-Naphthoic acids, copper and nickel salts, 263.
$C_{11}H_{10}O$ Styrylethinylcarbinol, 735.
$C_{11}H_{10}O_2$ Acetylphenylethinylcarbinol, 734.
$C_{11}H_{10}N_2$ 4-Anilinopyridine, 726.
$C_{11}H_{12}O$ 1-Methyl-β-tetralone, 690.
$C_{11}H_{12}O_2$ 5-Methoxy-β-tetralone, 690.
$C_{11}N_{12}O_4$ 3-Propenyl-4:6-dimethoxytoluquinone, 578.
$C_{11}H_{13}N_3$ *N*-Methyl-lepidylamine, and its dihydrochloride, 431.
$C_{11}H_{13}N$ 3-Propylindoles, 681.
$C_{11}H_{14}O$ Phenyl αγ-dimethylallyl ether, 558.
$C_{11}H_{14}O_2$ *p*-*n*-Butylbenzoic acid, 308.
$C_{11}H_{14}O_4$ 3-*n*-Propyl-4:6-dimethoxytoluquinone, 578.
$C_{11}H_{16}O_2$ *o*-β-Hydroxyethylbenzyl ethyl ether, 739.
$C_{11}H_{18}O$ Dihydrojasmone, spectrum of, 486.
$C_{11}H_{18}O_2$ Tetrahydropyrethrolone, spectrum of, 486.
$C_{11}H_{25}N$ *n*-Amylhexylamine, and its hydrochloride, 403.
Dimethylnonylamine, 403.
Ethylnonylamine, and its hydrochloride, 403.

11 III

$C_{11}H_6O_2Br_2$ Dibromo-5-methoxy-1:4-naphthaquinones, 238.
$C_{11}H_7O_2Br$ 2-Bromo-5-methoxy-1:4-naphthaquinone, 238.
$C_{11}H_7NS$ α-Naphthylthiocarbamide, addition of chlorine to, 374.
$C_{11}H_8O_2Br_2$ Dibromo-5-methoxy-1-naphthols, 237.
$C_{11}H_9O_2Br$ 2-Bromo-5-methoxy-1-naphthol, 238.
$C_{11}H_{10}ON_2$ Cinchoninomethylamide, 431.
$C_{11}H_{10}O_3S$ 6-Ethoxythio-oxindole-3-aldehyde, 414.
$C_{11}H_{11}O_3Cl_3$ 3-βββ-Trichloro-α-acetoxyethyl-*p*-cresol, 719.
$C_{11}H_{11}O_4N_3$ 2-Pyrrolidone-5-carboxy-*p*-nitroanilide, 243.
$C_{11}H_{11}O_5Cl$ 6-Chloromethyl-4-hydroxy-3:5-dimethoxyphthalide, 727.
$C_{11}H_{11}O_5N_3$ *N*-3:5-Dinitrobenzoyltetrahydro*iso*oxazine, 433.
$C_{11}H_{12}ON_2$ 2-Amino-6-methoxylepidine, 383.
4-Amino-6- and -8-methoxyquinaldines, 382.
$C_{11}H_{12}O_2N_2$ α-Phenylcrotonylcarbamide, 222.
$C_{11}H_{14}O_5S$ *O*-β-Phenylpropionylisethionic acid, sodium salt, 717.
$C_{11}H_{14}O_8N_4$ *N*-Methyl*iso*oxazolidine methopicrate, 433.
$C_{11}H_{15}O_2N$ *cyclo*Hexane-1:1-diacetomethylimide, 495.
$C_{11}H_{15}O_2N_3$ γ-Phenoxybutaldehyde semicarbazone, 424.
$C_{11}H_{17}N_3S$ Eucarvone thiosemicarbazone, 486.
$C_{11}H_{26}N_2I$ ββ-Bisdimethylaminomethyl-*N*-methyltrimethyleneimine methiodide, 178.

11 IV

$C_{11}H_5NCl_2S$ 2:4′-Dichloronaphtha(1′:2′:4:5)thiazole, 375.
$C_{11}H_6O_2NCl$ 6-Chloroquinoline-2:4-dicarboxylic acid, 428.
$C_{11}H_6NClS$ 4-Chloro-α-naphthylthiocarbimide, 374.
$C_{11}H_8O_2NCl$ Methyl 6-chlorocinchoninate, 429.
$C_{11}H_{10}O_8N_5Cl$ *N*-(2:4-Dinitrophenyl)-1:4-dimethylglyoxalinium chloride, 386.
$C_{11}H_{11}O_4N_3Cl$ *N*-(Dinitrophenyl)-1:4-dimethylglyoxalinium chlorides, 386.
$C_{11}H_{13}O_2NS$ Ethyl *p*-thioacetamidobenzoate, 641.
$C_{11}H_{13}O_3N_2Br$ α-(Bromophenyl)butyrylcarbamide, 223.
$C_{11}H_{12}O_3N_2S$ 1-Phenyl-2:3-dimethyl-5-pyrazolone-*x*-sulphonamide, and its sodium salt, 243.
$C_{11}H_{14}O_4N_2S$ Sulphanilylglutamic acid, and its sodium salt, 242.

C_{12} Group.

$C_{12}H_{10}O_2$ 2-Keto-5-styryl-2:3-dihydrofuran, 34.
$C_{12}H_{14}O_3$ 2-Keto-5-β-phenylethyltetrahydrofuran, 34.
$C_{12}H_{14}O_3$ ε-Phenoxy-Δ^{α}-hexenoic acid, 424.
$C_{12}H_{15}N$ 3-*n*-Butylindole, 682.
$C_{12}H_{16}O_2$ *p*-*n*-Amylbenzoic acid, 308.
$C_{12}H_{16}O_4$ 3-*iso*Butyl-4:6-dimethoxytoluquinone, 578.
$C_{12}H_{18}O$ 1-Ethinylgeraniol, 733.
$C_{12}H_{18}O_8$ *n*-Octane-αδεθ-tetracarboxylic acid, 518.
$C_{12}H_{18}Br_4$ $\Delta^{2'}$-*cyclo*Hexenyl-Δ^{2}-*cyclo*hexene tetrabromide, 518.
$C_{12}H_{22}O_4$ β-Methyl-β-*n*-hexylglutaric acid, 494.
$C_{12}H_{24}O_7$ Pentamethyl methyl-*d*-galactonate, 753.
$C_{12}H_{27}N$ Propylnonylamine, and its hydrochloride, 403.

12 III

$C_{12}H_7O_2N_3$ 1-Nitrophenazine, 502.
$C_{12}H_7O_4Br$ 2-Bromo-5-acetoxy-1:4-naphthaquinone, 238.
$C_{12}H_8O_2Br_2$ 2:4-Dibromo-5-acetoxy-1-naphthol, 237.
$C_{12}H_9O_4N_3$ 4(5)-Nitro-5(4)-3′:4′-methylenedioxystyrylglyoxaline, 233.
$C_{12}H_{10}O_2N_2$ 2-Anilinonicotinic acid, 726.
N-(Pyridyl)anthranilic acids, 726.
$C_{12}H_{10}O_2Br_2$ Dibromo-1:5-dimethoxynaphthalenes, 237.
$C_{12}H_{11}O_2N$ Vinylethinylcarbinol phenylurethane, 735.
$C_{12}H_{11}O_2N_3$ Nitrostyryl-1-methylglyoxalines, 235.
$C_{12}H_{12}O_2N_2$ 5-Acetamido-4-hydroxy-2-methylquinoline, 215.
$C_{12}H_{12}O_3N_2$ Ethyl 7-amino-2-hydroxyquinoline-4-carboxylate, 216.
$C_{12}H_{13}O_3Cl$ 6-Chloromethyl-3:4:5-trimethoxyphthalide, 726.
$C_{12}H_{14}ON_2$ 2-Amino-6-ethoxylepidine, 383.
$C_{12}H_{14}O_2N_2$ 2-Pyrrolidone-5-carboxy-*m*-toluidide, 243.
$C_{12}H_{14}O_5S$ *O*-Acetylmandelylisethionic acid, sodium salt, 718.
$C_{12}H_{15}ON_3$ 1-Methyl-β-tetralone semicarbazone, 690.
$C_{12}H_{16}O_4N_4$ *N*-Methyltetrahydro*iso*oxazine methopicrate, 433.
$C_{12}H_{16}O_8N_4$ Acetonyltrimethylammonium picrate, 174.
$C_{12}H_{17}ON$ *p*-*n*-Butylphenyl methyl ketoxime, 308.
$C_{12}H_{20}O_5N_2$ 6:6-Diethoxyhex-4-yn-3-ol urethane, 736.
$C_{12}H_{21}O_4N$ Ethyl pyrrolidine-1:2-diacetate, 426.
$C_{12}H_{23}O_6N$ 2-Acetamido-3:4:6-trimethyl β-methylglucoside, 553.
$C_{12}H_{26}NI$ Dimethylnonylamine methiodide, 403.
$C_{12}H_{29}N_3I_2$ ββ-Bisdimethylaminomethyl-*N*-methyltrimethyleneimine dimethiodide, 178.

12 IV

$C_{12}H_6O_3N_2Cl_2$ 2:4-Dichloro-5-nitroaceto-1-naphthalide, 724.
$C_{12}H_6O_3N_2Br_2$ 2:4-Dibromo-5-nitroaceto-1-naphthalide, 724.
$C_{12}H_9ON_2Br$ 3-Bromo-4-benzeneazophenol, 435.
$C_{12}H_9ON_2I$ 3-Iodo-4-benzeneazophenol, 435.
$C_{12}H_9O_2N_2Cl$ 2-Chloro-2′-nitrodiphenylamine, 505.
$C_{12}H_9O_3ClS$ 2-Chloro-1-naphthylthioglycollic acid, 415.
$C_{12}H_9O_3N_2Br$ 2-Bromo-5-nitroaceto-1-naphthalide, 724.
$C_{12}H_9O_3N_2I$ 2-Iodo-5-nitroaceto-1-naphthalide, 724.
$C_{12}H_9O_4N_2S$ 4-Nitrobenzenesulphon-4′-nitroanilide, 244.
$C_{12}H_{10}O_4N_2Hg$ 5-Nitro-1-naphthylamine-2-mercuriacetate, 724.
$C_{12}H_{10}O_5N_2S$ 4-*p*-Nitrophenoxybenzenesulphonamide, 242.
$C_{12}H_{10}Cl_4AlAs$ Trichlorodiphenylchloroarsinealuminium, 669.
$C_{12}H_{11}O_7N_3S_2$ *p*-Nitrophenoxybenzenedisulphonamide, 242.
$C_{12}H_{12}O_2N_2S$ Aminohydroxybenzenesulphonanilides, 709.
$C_{12}H_{14}O_4N_4S_2$ *s*-Di-*p*-aminobenzenesulphonhydrazide, 740.
$C_{12}H_{15}O_2N_3S$ 1-*p*-Aminobenzenesulphonamido-2:5-dimethylpyrrole, 726.
$C_{12}H_{15}O_4N_3S$ 2-Pyrrolidone-5-carboxyamino-3′-methylbenzene-*x*-sulphonamide, 243.
$C_{12}H_{16}O_5N_2S$ Sulphanilyladipamide, 241.
$C_{12}H_{30}ON_2I_2$ αγ-Bisdimethylamino-β-ethoxy-β-methylpropane dimethiodide, 172.

12 V

$C_{12}H_{10}O_6N_2I_2S_2$ 5:5-Di-iodobenzidine-2:2′-disulphonic acid, sodium salt, 716.

C_{13} Group.

$C_{13}H_8N_2$ 3-Cyanocarbazole, 502.
$C_{13}H_{10}O_2$ Phenyl carbonate, parachor and structure of, 661.
$C_{13}H_{10}O_4$ 4-(4′-Hydroxyphenoxy)benzoic acid, 349.
$C_{13}H_{10}O_5$ 3-Hydroxy-4-(4′-hydroxyphenoxy)benzoic acid, 350.
$C_{13}H_{10}F_2$ *pp*′-Difluorodiphenylmethane, 568.
$C_{13}H_{14}O_2$ 2:5-Dimethoxy-1-methylnaphthalene, 690.
$C_{13}H_{14}N_2$ 7-Amino-1:2:3:4-tetrahydroacridine, and its picrate, 696.
$C_{13}H_{16}O_2$ 5-Methoxy-1:1-dimethyl-β-tetralone, 691.
$C_{13}H_{16}O_3$ 2-Keto-5-β-*p*-methoxyphenylethyltetrahydrofuran, 35.
$C_{13}H_{16}O_5$ ε-Phenoxypentane-αβ-dicarboxylic acid, 423.
$C_{13}H_{18}O_2$ *p*-*n*-Hexylbenzoic acid, 308.
$C_{13}H_{24}O_2$ Brassylic semialdehyde, 482.
$C_{13}H_{32}N_4$ Tetrakisdimethylaminomethylmethane, 168; formation and thermal decomposition of salts of, 175.
$C_{13}H_{33}N$ Benzyl-*n*-propylnonylamine, 403.

13 III

$C_{13}H_8O_4N_4$ 2:4-Dimethylpent-2-enal 2:4-dinitrophenylhydrazone, 732.
$C_{13}H_8O_2Cl_2$ 2:5-Dichloro-4′-hydroxybenzophenone, 356.
$C_{13}H_8O_2S$ Benzthio-oxindole-3-aldehydes, 414.
$C_{13}H_9ON$ 4-Cyanodiphenyl ether, 113.
$C_{13}H_9N_2Cl$ Chloroaminoacridines, 379.
Chloromethylpyridoquinolines, 215.
$C_{13}H_{10}ON_2$ Hydroxymethylpyridoquinolines, 216.
$C_{13}H_{10}O_3Br_2$ Dibromoacetoxymethoxynaphthalenes, 237.

$C_{13}H_{10}O_4S$ 3-Carboxynaphthyl-2-thioglycollic acid, 410.
$C_{13}H_{11}NBr_2$ 4:4′-Dibromobenzhydrylamine, and its hydrochloride, 372.
$C_{13}H_{13}ON_3$ 4-Amidinodiphenyl ether, 110.
$C_{13}H_{12}O_2N_2$ 7-Nitro-1:2:3:4-tetrahydroacridine, and its picrate, 696.
$C_{13}H_{13}O_3N_3$ 2-*p*-Anisidinonicotinic acid, 726.
$C_{13}H_{12}NCl$ Chloro-1:2:3:4-tetrahydroacridines, and their picrates, 695.
$C_{13}H_{12}NBr$ Bromo-1:2:3:4-tetrahydroacridines, and their picrates, 695.
$C_{13}H_{12}NI$ 7-Iodo-1:2:3:4-tetrahydroacridine, and its picrate, 696.
$C_{13}H_{12}N_2I_2$ 3:3′-Di-iodo-4:4′-diaminodiphenylmethane, 715.
$C_{13}H_{13}ON$ 7-Hydroxy-1:2:3:4-tetrahydroacridine, and its picrate, 696.
$C_{13}H_{13}O_2N$ Propenylethinylcarbinol phenylurethane, 734.
$C_{13}H_{14}O_3N$ 1-(Nitrophenyliminomethyl)*cyclo*hexan-2-ones, 696.
$C_{13}H_{14}O_4N_4$ 3-Methylsorbic aldehyde 2:4-dinitrophenylhydrazone, 737.
$C_{13}H_{14}O_5Br_2$ Dibromo-ε-phenoxypentane-αβ-dicarboxylic acid, 423.
$C_{13}H_{15}O_2N$ 1-(*p*-Hydroxyphenyliminomethyl)*cyclo*hexan-2-one, 696.
$C_{13}H_{15}O_3N$ ε-Phenoxypentane-αβ-dicarboxyimide, 423.
$C_{13}H_{15}O_4N$ *dl*-γ-Methyl-α-ethylallyl *p*-nitrobenzoate, 26.
$C_{13}H_{17}O_2N_3$ 5-Methoxy-1-methyl-β-tetralone semicarbazone, 690.
$C_{13}H_{19}ON$ *p*-*n*-Amylphenyl methyl ketoxime, 308.
$C_{13}H_{19}ON_3$ *p*-*n*-Butylphenyl methyl ketone semicarbazone, 308.
$C_{13}H_{19}O_2N$ Ethylpropylcarbinol phenylurethane, 735.
$C_{13}H_{23}O_5N_3$ 6:6-Diethoxy-3-methylhex-4-yn-3-ol urethane, 736.

13 IV

$C_{13}H_4OBr_2D_4$ 4:4′-Dibromo-2:3:5:6-tetradeuterobenzophenone, 372.
$C_{13}H_6O_2N_2Cl_2$ Dichloronitroacridines, 380.
$C_{13}H_7O_3N_2Cl$ 3-Chloro-3-nitroacridone, 380.
$C_{13}H_7O_3N_2Cl$ 4-Nitro-*C*-(*p*-chlorophenyl)anthranil, 380.
$C_{13}H_7O_4N_2Cl$ 8-Chloro-2-nitro-10-hydroxyacridone, 380.
$C_{13}H_7NBr_2D_4$ 4:4′-Dibromo-2:3:5:6-tetradeuterobenzhydrylamine, 372.
$C_{13}H_6O_2N_2Br$ 7-Bromo-1-phenylbenztriazole-5-carboxylic acid, 505.
$C_{13}H_8O_3N_2Cl_2$ 2:5-Dichlorobenz-*m*-nitroanilide, 356.
$C_{13}H_9ON_2Cl$ 8-Chloro-2-aminoacridone, 381.
$C_{13}H_9O_4N_2Cl$ Chloronitrodiphenylamine-2-carboxylic acids, 379.
$C_{13}H_9O_4N_2Br$ 2-Bromo-6-nitrodiphenylamine-4-carboxylic acid, 505.
$C_{13}H_{11}O_2N_2Br$ 2-Bromo-6-aminodiphenylamine-4-carboxylic acid, 505.
$C_{13}H_{11}O_2N_3S$ 2-Aminoacridine-7-sulphonamide, 183.
$C_{13}H_{12}O_3N_2S$ N^4-Benzoylsulphanilamide, 241.
$C_{13}H_{13}O_4N_2S$ 5:6:2′:3′-Pyridoquinolinium methyl sulphate, 217.
$C_{13}H_{14}ONCl$ 1-(Chlorophenyliminomethyl)*cyclo*hexan-2-ones, 695.
$C_{13}H_{14}ONBr$ 1-(Bromophenyliminomethyl)*cyclo*hexan-2-ones, 696.
$C_{13}H_{14}ONI$ 1-(*p*-Iodophenyliminomethyl)*cyclo*hexan-2-one, 696.
$C_{13}H_{14}O_8N_4S$ 2:4:5-Trinitro-*p*-toluenesulphon-1-naphthalide, 724.
$C_{13}H_{16}O_2N_2S$ 1-*p*-Toluenesulphonamido-2:5-dimethylpyrrole, 726.

13 V

$C_{13}H_{16}O_2N_3BrS$ Sulphanilylaminoethylpyridinium bromide, 242.

C_{14} Group.

$C_{14}H_{12}$ αα-Diphenylethylene, structure of, 567.

14 II

$C_{14}H_7N_3$ 3:6-Dicyanocarbazole, 502.
$C_{14}H_8N_4$ 4:4′-Dicyanoazobenzene, 112.
$C_{14}H_{10}O_2$ Benzil, structure of, 661.
$C_{14}H_{10}Cl_2$ αα-Di-*p*-chlorophenylethylene, 568.
$C_{14}H_{10}Br_2$ αα-Di-*p*-bromophenylethylene, 568.
$C_{14}H_{10}F_2$ αα-Di-*p*-fluorophenylethylene, 568.
$C_{14}H_{11}N_3$ 4-Amidino-2′-cyanodiphenyl, 110.
$C_{14}H_{12}O_2$ 2:7-Dihydroxy-9:10-dihydrophenanthrene, 687.
$C_{14}H_{12}O_4$ Hydroxy-4-(4′-hydroxyphenoxy)acetophenones, 350, 351.
4-(4′-Methoxyphenoxy)benzoic acid, 349, 352.
4-Phenoxy-2-methoxybenzoic acid, 352.
$C_{14}H_{14}O_2$ 3:3′-Dihydroxydibenzyl, 687.
$C_{14}H_{14}N_8$ 4:4′-Diamidinoazobenzene, dihydrochloride of, 111.
$C_{14}H_{15}N$ Methyl-1:2:3:4-tetrahydroacridines, and their picrates, 695.
$C_{14}H_{16}N_6$ 4:4′-Diamidinodiphenylamine, salts of, 111, 116.
$C_{14}H_{16}O_5$ 1-Hydroxy-1-γ-ketobutyl-2-keto-1:2:3:4-tetrahydronaphthalene, 688.
$C_{14}H_{16}O_4$ γ-Methyl-α-ethylallyl hydrogen phthalates, 24.
$C_{14}H_{16}O_7$ ε-Phenoxypentane-αββ-tricarboxylic acid, 423.
$C_{14}H_{18}O_4$ *dl*-Ethyl-*n*-propylcarbinyl hydrogen phthalate, 25.
$C_{14}H_{20}O_2$ Acetyl-1-ethinylgeraniol, 733.
p-*n*-Heptylbenzoic acid, 308.
1-(γ-Hydroxybutyl)-2-hydroxy-1:2:3:4-tetrahydronaphthalene, 688.
$C_{14}H_{22}O$ Irone, absorption spectrum of, 95.
3-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-1-methylcrotonaldehyde, 732.

$C_{14}H_{24}O$ 4:7-Dimethyl-2-*iso*propyl-5-hydrindanone, 561.
Perhydro-2-methyl-5:6-benzochroman, 688.
$C_{14}H_{24}O_3$ β-(2-Acetyl-4-*iso*propyl*cyclo*pentyl)butyric acid, 562.
$C_{14}H_{26}O$ *n*-Amyl β-*n*-amyl*iso*propenyl ketone, 496.
$C_{14}H_{26}O_3$ Methyl brassylate semialdehyde, 482.
$C_{14}H_{28}O_2$ 2:2-Dimethyl-lauric acid, 492.

14 III

$C_{14}H_8ON_2$ 4:4′-Dicyanodiphenyl ether, 113.
$C_{14}H_8O_6N_2$ 1-Nitrocarbazole-3:6-dicarboxylic acid, 503.
$C_{14}H_8N_2S$ 4:4′-Dicyanodiphenyl sulphide, 113.
$C_{14}H_9N_2Cl$ *N*-4-Cyanophenylbenziminochloride, 116.
$C_{14}H_9N_2Br$ 6-Bromo-4-phenylcinnoline, 355.
$C_{14}H_{10}ON_2$ 2′-Ketopiperazino(6′:4′:1:9)carbazole, 505.
$C_{14}H_{10}O_2Cl_2$ 2:5-Dichloro-2′-hydroxy-5′-methylbenzophenone, 357.
$C_{14}H_{10}O_2N_2$ 1-Nitro-9-acetylcarbazole, 502.
$C_{14}H_{10}O_8N_4$ 3:5-Dihydroxy-2-formylbenzoic acid 2:4-dinitrophenylhydrazone, 369.
$C_{14}H_{11}OCl$ 4-Chloro-4′-acetoxydiphenyl, 583.
$C_{14}H_{12}OS$ Desylthiol, 93.
$C_{14}H_{12}NBr$ α-Phenyl-α-(5-bromo-2-aminophenyl)ethylene, sulphate of, 355.
$C_{14}H_{13}O_2N$ 1:2:3:4-Tetrahydroacridine-7-carboxylic acid, 696.
$C_{14}H_{13}N_3S$ *p*-Thioacetamidoazobenzene, 641.
$C_{14}H_{14}N_4S$ 4:4′-Diamidinodiphenyl sulphide, 110.
$C_{14}H_{14}N_4S_2$ 4:4′-Diamidinodiphenyl disulphide, dihydrochloride of, 111.
$C_{14}H_{15}ON$ Methoxy-1:2:3:4-tetrahydroacridines, and their picrates, 696.
$C_{14}H_{15}O_2N$ *iso*Butenylethinylcarbinol phenylurethane, 735.
$C_{14}H_{15}O_2N$ 1-(*o*-Carboxyphenyliminomethyl)*cyclo*hexan-2-one, 696.
$C_{14}H_{16}ON_2$ Cinchoninodiethylamide, and its picrate, 431.
$C_{14}H_{17}ON$ 1-(Phenyliminomethyl)-4-methyl*cyclo*hexan-2-one, 695.
1-(Tolyliminomethyl)*cyclo*hexan-2-ones, 695.
$C_{14}H_{17}O_2N$ 1-(Methoxyphenyliminomethyl)*cyclo*hexan-2-ones, 696.
$C_{14}H_{19}ON_2$ 2:4-Dimethylpent-2-enal phenylsemicarbazone, 732.
$C_{14}H_{19}O_2N_3$ 5-Methoxy-1:1-dimethyl-β-tetralone semicarbazone, 691.
$C_{14}H_{21}ON$ *p*-*n*-Hexylphenyl methyl ketoxime, 308.
$C_{14}H_{21}ON_3$ *p*-*n*-Amylphenyl methyl ketone semicarbazone, 308.
$C_{14}H_{25}O_2N$ β-Methyl-β-*n*-octylglutarimide, 494.
$C_{14}H_{27}O_2N_3$ Brassylic semialdehyde semicarbazone, 482.

14 IV

$C_{14}H_8O_2N_2S$ 4:4′-Dicyanodiphenylsulphone, 113.
$C_{14}H_9ON_2Cl$ 6-Chloro-4-(4′-hydroxyphenyl)cinnoline, 357.
$C_{14}H_9O_2N_2S$ 4:4′-Dicyanobenzenesulphonanilide, 115.
$C_{14}H_9O_4N_2Cl$ 8-Chloro-2-nitro-10-methoxyacridone, 381.
$C_{14}H_{10}O_2NCl$ Chloromethoxyanthroxan, 356.
$C_{14}H_{11}ONBr_2$ Formo-4:4′-dibromobenzhydrylamide, 372.
$C_{14}H_{11}ON_2Br$ 1-ω-Bromoacetamidocarbazole, 505.
$C_{14}H_{11}O_4N_2Br$ Methyl 2-bromo-6-nitrodiphenylamine-4-carboxylate, 505.
$C_{14}H_{12}ONCl$ α-(5-Chloro-2-aminophenyl)-α-(4′-hydroxyphenyl)ethylene, 356.
$C_{14}H_{12}O_2NCl$ 5-Chloro-2-amino-4′-methoxybenzophenone, 356.
$C_{14}H_{12}O_5N_2S$ 4-Amino-4′-carboxyformamidodiphenylsulphone, 43.
$C_{14}H_{13}O_3NS$ 1-Acetamido-1-naphthylthioglycollic acid, 415.
$C_{14}H_{14}ONBr$ Phenyl-(5-bromo-2-aminophenyl)methylcarbinol, 355.
$C_{14}H_{14}O_2N_4S$ 4:4′-Diamidinodiphenylsulphone, dihydrochloride of, 110.
$C_{14}H_{16}O_2N_2S$ 4:4′-Diamidinobenzenesulphonanilide, dihydrochloride of, 111.

14 V

$C_{14}H_7ONBr_2D_4$ Formo-4:4-dibromo-2:3:5:6-tetradeuterobenzhydrylamide, 372.

C_{15} Group.

$C_{15}H_{18}$ Vetivazulene, synthesis of, 559.
$C_{15}H_{26}$ Dihydrofarnesene, 120.

15 II

$C_{15}H_{11}N$ 4-Cyanostilbene, 112.
$C_{15}H_{12}O_2$ 2-Hydroxy-7-methoxyphenanthrene, 686.
$C_{15}H_{12}O_4$ Diphenylmethane-2:4′-dicarboxylic acid, 210.
$C_{15}H_{12}O_5$ 4-(4′-Acetoxyphenoxy)benzoic acid, 349.
$C_{15}H_{13}N$ 3-Benzylindole, 682.
2:3-Dimethyl-5:6-benzoquinoline, and its picrate, 695.
$C_{15}H_{14}O_2$ 2-Hydroxy-7-methoxy-9:10-dihydrophenanthrene, 687.
$C_{15}H_{14}O_3$ 4-(4′-Methoxyphenoxy)acetophenone, 351.
$C_{15}H_{14}O_4$ Ethyl 4-(4′-hydroxyphenoxy)benzoate, 349.
β-4-(4′-Hydroxyphenoxy)phenylpropionic acid, 352.
4-*m*-Methoxyphenylacetylresorcinol, 688.
$C_{15}H_{14}O_5$ Ethyl 3-hydroxy-4-(4′-hydroxyphenoxy)benzoate, 350.
3-Methoxy-4-(4′-methoxyphenoxy)benzoic acid, 350.

$C_{15}H_{15}N_3$ 4-Amidinostilbene, hydrochloride of, 110.
$C_{15}H_{15}N_3$ 4-Amino-4′-amidinostilbene, dihydrochloride of, 110.
$C_{15}H_{16}O_2$ 2-Hydroxy-7-methoxy-1:2:3:4-tetrahydrophenanthrene, 687.
p-Methoxybenzhydryl methyl ether, 609.
$C_{15}H_{16}O_6$ Ethyl 3:4:5-trimethoxyphthalidylglyoxylate, 727.
$C_{15}H_{17}N$ 6:9-Dimethyl-1:2:3:4-tetrahydroacridine, and its picrate, 695.
$C_{15}H_{19}N$ 3-*cyclo*Hexyl-7-methylindole, 682.
$C_{15}H_{21}N$ 3-*n*-Heptylindole, 682.
$C_{15}H_{25}N$ Benzylethylhexylamine, 403.
$C_{15}H_{26}O_3$ α-Methyl-α-*n*-decylsuccinic anhydride, 495.
$C_{15}H_{26}O$ Dihydronerolidol, 119.
$C_{15}H_{29}Cl_3$ Dihydrofarnesene trihydrochloride, 120.

15 III

$C_{15}H_8ON_2$ 4:4′-Dicyanobenzophenone, 111.
$C_{15}H_9ON_3$ 4:4′-Dicyanobenzanilide, 115.
$C_{15}H_{10}ON_2$ 3-Cyano-9-acetylcarbazole, 502.
Cyanophenyl 4-cyanobenzyl ethers, 113.
4:4′-Dicyanobenzhydrol, 111.
$C_{15}H_{10}O_2N_2$ 4:4′-Dicyanodiphenoxymethane, 114.
4-Nitro-4′-cyanostilbene, 112.
$C_{15}H_{10}O_3N_2$ 8-Quinolyl *p*-nitrophenyl ether, 242.
$C_{15}H_{11}ON$ 4-Phenoxyquinoline, and its salts, 383.
$C_{15}H_{11}O_3N_3$ 2-Nitro-4-cyanophenyl 4-nitro-β-phenylethyl ether, 115.
$C_{15}H_{12}O_2N_2$ 4-Cyanobenzyl phenylurethane, 114.
$C_{15}H_{13}O_2N_3$ 2:4′-Dihydroxy-4-4″-iminazolyldiphenyl ether, and its picrate, 350.
$C_{15}H_{12}O_9N_4$ Methyl 3:5-dihydroxy-2-formylbenzoate 2:4-dinitrophenylhydrazone, 369.
$C_{15}H_{13}ON$ 4-Cyanophenyl β-phenylethyl ether, 115.
$C_{15}H_{13}O_3N_3$ 4-Nitro-4′-amidinostilbene, hydrochloride of, 110.
$C_{15}H_{14}ON_4$ 4:4′-Diamidinobenzophenone, dihydrochloride of, 110.
$C_{15}H_{14}O_2N_2$ 2-Pyrrolidone-5-carboxy-α-naphthalide, 243.
$C_{15}H_{14}O_6N_2$ Ethyl 3-*p*-nitrobenzoyloxy-4-methylpyrrole-2-acetate, 426.
$C_{15}H_{15}ON$ Acetyl-1:2:3:4-tetrahydroacridine, and its picrate, 696.
3-(Naphthyliminomethyl)butan-2-ones, 695.
$C_{15}H_{15}ON_3$ 4:4′-Diamidinobenzanilide, 111.
$C_{15}H_{15}O_2N_3$ 4-Nitro-2-benzylideneaminodimethylaniline, 756.
$C_{15}H_{15}O_3N_3$ 4-(4′-Methoxyphenoxy)benzaldehyde semicarbazone, 353.
$C_{15}H_{15}NS$ Thioacetobenzylanilide, 641.
$C_{15}H_{16}ON_2$ 7-Acetamido-1:2:3:4-tetrahydroacridine, 696.
$C_{15}H_{16}ON_4$ Amidinophenyl 4-amidinobenzyl ethers, dihydrochlorides of, 110.
4:4′-Diamidinobenzhydrol, dihydrochloride of, 110.
$C_{15}H_{16}ON_6$ 4:4′-Diamidinodiphenylurea dimethanesulphonate, 111.
$C_{15}H_{16}O_2N_4$ 4:4′-Diamidinodiphenoxymethane, dihydrochloride of, 110.
$C_{15}H_{17}O_2N$ 1-(*m*-Acetylphenyliminomethyl)*cyclo*hexan-2-one, 696.
$C_{15}H_{17}O_3N$ 1-(*o*-Carbomethoxyphenyliminomethyl)*cyclo*hexan-2-one, 696.
$C_{15}H_{19}ON$ 1-(*p*-Xylyliminomethyl)*cyclo*hexan-2-one, 695.
$C_{15}H_{23}ON$ *p*-*n*-Heptylphenyl methyl ketoxime, 308.
$C_{15}H_{23}ON_3$ *p*-*n*-Hexylphenyl methyl ketone semicarbazone, 308.
$C_{15}H_{25}N_3S$ 3-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-1-methylcrotonaldehyde thiosemicarbazone, 732.
$C_{15}H_{27}O_2N$ α-Methyl-α-*n*-decylsuccinimide, 495.
$C_{15}H_{27}O_3N_3$ β-(2-Acetyl-4-*iso*propyl*cyclo*pentyl)butyric acid semicarbazone, 562.

15 IV

$C_{15}H_9O_2NBr$ 3:5-Dibromo-6-methoxyphthalanil, 239.
$C_{15}H_{10}O_2NBr$ 5-Bromo-6-methoxyphthalanil, 239.
$C_{15}H_{11}ON_2Cl$ 6-Chloro-4-(2′-hydroxy-5′-methylphenyl)cinnoline, 358.
$C_{15}H_{12}O_2NCl$ 5-Chloro-2-amino-2′-methoxyanthroxan, 357.
$C_{15}H_{13}O_2N_2Br$ 2-Bromo-6-acetamidodiphenylamine-4-carboxylic acid, 505.
$C_{15}H_{14}ONCl$ α-(5-Chloro-2-aminophenyl)-α-(2′-hydroxy-5′-methylphenyl)ethylene, 357.
$C_{15}H_{14}O_2NCl$ 5-Chloro-2-amino-2′-methoxy-5′-methylbenzophenone, 357.
$C_{15}H_{14}O_4N_2S$ 4-Benzylideneaminobenzenesulphonylglycine, 242.
$C_{15}H_{15}O_3NS$ *p*-(2-1:2:3:4-Tetrahydro*iso*quinolyl)benzenesulphonic acid, 740.
$C_{15}H_{16}O_2N_2S$ 2-*p*-Aminobenzenesulphonyl-1:2:3:4-tetrahydro*iso*quinoline, 739.
p-(2-1:2:3:4-Tetrahydro*iso*quinolyl)benzenesulphonamide, 740.
$C_{15}H_{16}O_6N_2S$ Pyridine acetamidoacetoxybenzenesulphonates, 709.
$C_{15}H_{17}O_4N_5S_2$ Disulphanilylethyleneguanidine, 241.

15 V

$C_{15}H_{14}O_5N_2SHg$ 2′-Acetoxymercuri-3′-hydroxybenzylidenesulphanilamide, 242.

C_{16} Group.

$C_{16}H_{18}$ 3-*tert.*-Butylacenaphthene, 563.

16 II

$C_{16}H_{10}N_2$ Dicyanostilbenes, 111, 112.
$C_{16}H_{12}O_4$ 2:7-Dihydroxy-9:10-dihydrophenanthrene-3:8-dicarboxylic acid, 687.

$C_{16}H_{13}N_3$ Quinoline-4-aldehyde anil, 431.
$C_{16}H_{14}O_2$ 3-*tert.*-Butylacenaphthenequinone, 564.
$C_{16}H_{14}O_3$ 4-*tert.*-Butylnaphthalic anhydride, 563.
$C_{16}H_{14}O_4$ 2-Hydroxy-7-methoxy-9:10-dihydrophenanthrene-3-carboxylic acid, 687.
4-(4′-Methoxyphenoxy)cinnamic acid, 352.
$C_{16}H_{14}O_5$ Methyl 2:4-dihydroxy-5-phenylacetylbenzoate, 687.
Methyl 2-hydroxy-4-phenylacetoxybenzoate, 687.
$C_{16}H_{14}N_2$ *N*-Phenyl-lepidylamine, 431.
$C_{16}H_{16}O_2$ 2:7-Dimethoxy-9:10-dihydrophenanthrene, 686.
$C_{16}H_{16}O_4$ Ethyl 5-phenoxy-2-methoxybenzoate, 352.
Methyl 2:4-dihydroxy-5-phenylethylbenzate, 688.
$C_{16}H_{16}N_4$ Diaminostilbenes, salts, 110.
$C_{16}H_{18}N_4$ 4:4′-Diamidinomethyldiphenyl, dihydrochloride of, 110.
4:4′-Dimethylamidinodiphenyl, dihydrochloride of, 110.
$C_{16}H_{22}O$ 1-Keto-3-*cyclo*hexenyl-Δ^2-octahydrophenanthrene, 395.
$C_{16}H_{24}O$ 6-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-4-methylhex-4-en-1-yn-2-ol, 733.
$C_{16}H_{24}O_2$ 12-Acetyl-9-ketotetradecahydrophenanthrenes, 394.
$C_{16}H_{15}N$ Benzylidenenonylamine, 403.
$C_{16}H_{27}N$ Benzyl-*n*-nonylamine, and its hydrochloride, 403.
Benzyl-*n*-propylhexylamine, 403.
$C_{16}H_{28}O_2$ 5-Methyl-2-butyl-5-*n*-amyl*cyclo*hexane-1:3-dione, 496.
$C_{16}H_{28}N_2$ α-Diethylamino-δ-amylbenzylamine, 427.
$C_{16}H_{29}N_3$ α-Diethylamino-δ-amyl-*m*-aminobenzylamine, 427.
$C_{16}H_{32}O_2$ 3:3-Dimethyltetradecoic acid, 494.
$C_{16}H_{34}O$ 1-Methyl-1-heptyloctan-1-ol, 493.

16 III

$C_{16}H_{10}ON_2$ 4:4′-Dicyanodeoxybenzoin, 115.
$C_{16}H_{12}ON_2$ Cinchoninanilide, 437.
4-Cyanophenyl 4-cyano-β-phenylethyl ether, 116.
ω-Cyano-*p*-tolyl 4-cyanobenzyl ether, 113.
4:4′-Dicyanodibenzyl ether, 114.
$C_{16}H_{12}O_2N_2$ 4:4′-Dicyano-αβ-diphenoxyethane, 114.
$C_{16}H_{12}O_4N_2$ ω-Diazo-4-(4′-acetoxyphenoxy)acetophenone, 349.
Phenylethinylcarbinol *p*-nitrophenylurethane, 734.
$C_{16}H_{13}ON$ 2-Phenoxylepidine, 383.
4-Phenoxyquinaldine, 383.
$C_{16}H_{13}ON_3$ 4:4′-Dicyano-β-phenoxyethylaniline, 114.
$C_{16}H_{13}O_2N$ Phenylethinylcarbinol phenylurethane, 734.
Vinylethinylcarbinol α-naphthylurethane, 735.
$C_{16}H_{13}N_2Cl$ *N*-Phenyl-6-chlorolepidylamine, 431.
$C_{16}H_{14}O_2N_2$ 4-Nitro-4′-acetamidostilbene, 112.
$C_{16}H_{15}O_2N$ 4-*tert.*-Butylnaphthalimide, 563.
$C_{16}H_{16}ON_4$ 4:4′-Diamidinodeoxybenzoin, dihydrochloride of, 110.
$C_{16}H_{16}O_2I_2$ 6:6′-Di-iodo-3:3′-dimethoxydibenzyl, 686.
$C_{16}H_{16}O_2S$ β-(Benzhydrylthio)propionic acid, 95.
$C_{16}H_{16}O_4N_4$ β-Phenylethyl methyl ketone dinitrophenylhydrazone, 62.
$C_{16}H_{17}O_2N$ Carbethoxy-1:2:3:4-tetrahydroacridines, and their picrates, 696.
$C_{16}H_{17}O_3N_3$ *N*-Nitroso-*p*-toluidinoaceto-*p*-toluidide, 54.
$C_{16}H_{17}O_3N_3$ β-*o*-Methoxyphenylpropaldehyde *p*-nitrophenylhydrazone, 182.
$C_{16}H_{17}O_4N_3$ *N*-Nitroso-*p*-anisidineaceto-*p*-anisidide, 54.
$C_{16}H_{17}N_2I$ 2-Anilinovinylquinoline methiodide, 712.
$C_{16}H_{17}N_3S$ 2-Thioacetamido-5:4′-dimethylazobenzene, 641.
$C_{16}H_{18}ON_4$ 4-Amidinomethylphenyl 4-amidinobenzyl ether, 110.
4-Amidinophenyl 4-amidino-β-phenylethyl ether, dihydrochloride of, 110.
4:4′-Diamidinodibenzyl ether, and its dihydrochloride, 110.
$C_{16}H_{18}O_2N_4$ 4:4′-Diamidino-αβ-diphenoxyethane, dihydrochloride of, 110.
$C_{16}H_{18}O_2N_4$ 4:4′-Diamidinodiphenoxydimethyl ether, and its dihydrochloride, 111.
$C_{16}H_{18}O_2S$ *p*-Tolyl-α-anisylethylsulphone, 610.
$C_{16}H_{19}O_2N$ 1-(Carbethoxyphenyliminomethyl)*cyclo*hexan-2-ones, 696.
$C_{16}H_{22}O_2N_2$ αα′-Dicyano-β-methyl-β-octylglutarimide, 494.
$C_{16}H_{21}ON_3$ *p*-*n*-Heptylphenyl methyl ketone semicarbazone, 308.
$C_{16}H_{25}O_2N$ 12-Acetyl-9-ketotetradecahydrophenanthrene oximes, 394.
$C_{16}H_{25}O_5N$ Tetramethyl *l*-galactose anilide, 754.
$C_{16}H_{26}O_2N_2$ Ethyl β-keto-αγ-di-(1-methyl-2-pyrrolidyl)butyrate dipicrate, 424.
$C_{16}H_{33}ON$ 1-Keto-3-*cyclo*hexenyl-Δ^2-octahydrophenanthrene oxime, 395.

16 IV

$C_{16}H_6O_4N_2Cl_4$ 1-Nitro-3:6-bistrichloroacetylcarbazole, 503.
$C_{16}H_9N_3Cl_2Br$ 2-Bromo-1-2′:5′-dichlorobenzeneazonaphthalene, 437.
$C_{16}H_{10}O_2NBr$ 6-Bromo-2-anilino-5-hydroxy-1:4-naphthaquinone, 238.
$C_{16}H_{10}N_2ClBr$ 2-Bromo-1-3′-chlorobenzeneazonaphthalene, 437.
$C_{16}H_{11}ON_2Cl$ 6-Chlorocinchoninanilide, 431.
$C_{16}H_{12}O_8N_2S$ 4:4′-Biscarboxyformamidodiphenylsulphone, 43.
$C_{16}H_{13}O_2NS$ 6-Ethoxythionaphthenquinone-2-*p*-hydroxyanil, 410.
$C_{16}H_{15}O_2N_3S$ N^1-Lepidylsulphanilamide, 428.
N^4-(2′-Lepidyl)sulphanilamide, 758.
N^4-(4′-Quinaldyl)sulphanilamide, 758.

$C_{16}H_{16}O_2NBr$ Phenyl-(5-bromo-2-acetamidophenyl)methylcarbinol, 355.
$C_{16}H_{16}O_4N_4S$ 2-(2′-Pyrrolidone-5′-carboxy-4″-aminobenzenesulphamido)pyridine, 243.
$C_{16}H_{16}O_4N_2S$ Acetamidoacetoxybenzenesulphonanilides, 709.
$C_{16}H_{17}O_2NS$ 2-*p*-Toluenesulphonyl-1:2:3:4-tetrahydro*iso*quinoline, 739.
$C_{16}H_{18}O_6N_4S_2$ *s*-Di-*p*-acetamidobenzenesulphonhydrazide, 740.

16 V

$C_{16}H_{11}O_{10}N_3I_2S_3$ 2-(2′:6′-Di-iodo-4′-sulphobenzeneazo)-1-amino-8-naphthol-3:6-disulphonic acid, trisodium salt, 716.
$C_{16}H_{13}ON_2ClS$ Chloromethylthio-oxindole-3-aldehyde phenylhydrazones, 414.
$C_{16}H_{14}O_3N_2ClS$ N^1-(6-Chlorolepidyl)sulphanilamide, 429.
$C_{16}H_{14}O_{10}N_2S_2As$ 1-(4′-Arsonobenzeneazo)-2-amino-8-naphthol-3:6-disulphonic acid, tetrapotassium salt, 715.

16 VI

$C_{16}H_{12}O_{10}N_3I_2S_2As$ 2-(2′:6′-Di-iodo-4′-arsonobenzeneazo)-1-amino-8-naphthol-3:6-disulphonic acid, tetrasodium salt, 715.

C_{17} Group.

$C_{17}H_{12}O_4$ Phenylethinylcarbinyl hydrogen phthalate, 734.
$C_{17}H_{14}O_7$ 3-Acetoxy-4-(4′-acetoxyphenoxy)benzoic acid, 350.
$C_{17}H_{14}N_2$ 4:4′-Dicyano-$\alpha\gamma$-diphenylpropane, 112.
$C_{17}H_{15}N$ 6:7:8:9-Tetrahydro-1:2-benzacridine, and its picrate, 695.
$C_{17}H_{16}O_4$ Methyl 4-(4′-methoxyphenoxy)cinnamate, 352.
$C_{17}H_{17}N$ 3-γ-Phenylpropylindole, 682.
$C_{17}H_{18}O_4$ Ethyl β-4-(4′-hydroxyphenoxy)phenylpropionate, 352.
Methyl β-4-(4′-methoxyphenoxy)phenylpropionate, 352.
$C_{17}H_{18}Cl_2$ 4:4′-Dichloromethyl-$\alpha\gamma$-diphenylpropane, 112.
$C_{17}H_{20}O_2$ 4:4′-Dihydroxymethyl-$\alpha\gamma$-diphenylpropane, 112.
$C_{17}H_{20}O_3$ 2:5:3′-Trimethoxydibenzyl, 687.
$C_{17}H_{20}N_4$ 4:4′-Diamidinodiphenylpropane, dihydrochloride of, 110.
$C_{17}H_{22}O_2$ *d*-6″-Hydroxy-2:2:5′:4″-tetramethyl-3′:4′:5′:6′-tetrahydrodibenzopyran, 187.
$C_{17}H_{24}O_2$ 2-Phenacyl-2-methyloctoic acid, 496.
$C_{17}H_{26}O$ 7-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-5-methylhepta-3:5-dien-2-one, 733.
$C_{17}H_{29}N$ Benzyl-*n*-butylhexylamine, 402.
$C_{17}H_{30}O_3$ 1-β-Ketononyl*cyclo*hexane-1-acetic acid, 495.
$C_{17}H_{32}O_2$ 5-Keto-3-methyl-3-*n*-hexylnonoic acid, 494.

17 III

$C_{17}H_{10}ON_2$ 4:4′-Dicyanobenzylideneacetophenone, 113.
$C_{17}H_{11}ON$ 9-Amino*meso*benzanthrone, 211.
$C_{17}H_{12}O_6N_2$ 4:4′-Dinitro-$\alpha\delta$-diphenylbutadiene-α-carboxylic acid, 112.
$C_{17}H_{14}O_2N_2$ 4:4′-Dicyano-$\alpha\gamma$-diphenoxypropane, 114.
$C_{17}H_{15}ON_3$ 2-Benzeneazo-6-methoxylepidine, 383.
4-Benzeneazo-6- and -8-methoxyquinaldines, 382.
$C_{17}H_{15}O_2N$ 2-Phenoxy-6-methoxylepidine, 383.
4-Phenoxy-6- and -8-methoxyquinaldines, 383.
Propenylethinylcarbinol β-naphthylurethane, 734.
$C_{17}H_{16}ON_4$ 4:4′-Diamidinobenzylideneacetophenone, dihydrochloride of, 110.
$C_{17}H_{16}O_2S$ β-Desylthiopropionic acid, 94.
$C_{17}H_{17}ON$ 1-(Naphthyliminomethyl)*cyclo*hexan-2-ones, 695.
$C_{17}H_{17}O_2N$ 4-*tert.*-Butylnaphthal-*N*-methylimide, 564.
$C_{17}H_{18}O_4N_4$ α-Benzyl-α-methylacetone dinitrophenylhydrazone, 63.
$C_{17}H_{20}O_2N_4$ 3:3′-Diamidino-$\alpha\gamma$-diphenoxypropane, dihydrochloride of, 110.
$C_{17}H_{25}ON_3$ 1-Keto-3-*cyclo*hexenyl-Δ^2-octahydrophenanthrene semicarbazone, 395.
$C_{17}H_{27}ON_3$ *p*-*n*-Octylphenyl methyl ketone semicarbazone, 308.
$C_{17}H_{30}ON_2$ α-Diethylamyl-δ-amyl-*p*-methoxybenzylamine, 427.

17 IV

$C_{17}H_9O_3ClS_2$ 5-Chloro-7-methylthioindigo, 412.
6-Chlorothioindirubin, 411.
$C_{17}H_{11}O_3NS$ 6:7-Benzthionaphthenquinone-2-*p*-hydroxyanil, 410.
$C_{17}H_{14}O_4N_2S$ 5-Nitro-*p*-toluenesulphon-1-naphthalide, 724.
$C_{17}H_{15}O_4N_3S$ N^4-Quininoylsulphanilamide, 243.
$C_{17}H_{16}O_2NCl$ 5-Chloro-2-acetamido-2′-methoxy-5′-methylbenzophenone, 357.
$C_{17}H_{17}ON_2Cl$ Substance, from furfural, aniline, and aniline hydrochloride, 506.
$C_{17}H_{17}ON_2I$ 2-Methylanilinovinylbenzoxazole ethiodide, 712.
$C_{17}H_{17}O_3N_3S$ N^1-(6-Methoxylepidyl)sulphanilamide, 428.
N^4-(6′-Methoxy-2′-lepidyl)sulphanilamide, 758.
N^4-(Methoxy-4′-quinaldyl)sulphanilamides, 758.
$C_{17}H_{17}N_2IS$ 2-Methylanilinovinylbenzthiazole methiodide, 712.
$C_{17}H_{18}O_2NCl$ 2-Chloro-4-*tert.*-butylphenyl *p*-nitrobenzyl ether, 678.
$C_{17}H_{18}O_3N_2S$ 2-*p*-Acetamidobenzenesulphonyl-1:2:3:4-tetrahydro*iso*quinoline, 739.
$C_{17}H_{19}O_3N_3S$ *p*-Acetamidobenzenesulphon-1-(1:2:3:4-tetrahydroquinolyl)amide, 740.
$C_{17}H_{22}O_4N_2S_2$ Methylenebis-*p*-toluenesulphonmethylamide, 30.
$C_{17}H_{23}O_4N_3S_2$ Bis(benzenesulphonmethylamidomethyl)methylamine, 30.

17 V

$C_{17}H_{10}O_2NClS$ Chloromethylthionaphthenindoleindigos, 414.
$C_{17}H_{11}O_9N_3I_2S_2$ 2-(2′:4′-Di-iodo-6′-carboxybenzeneazo)-1-amino-8-naphthol-3:6-disulphonic acid, trisodium salt, 716.
$C_{17}H_{14}O_7N_3IS_2$ 2-5′-Iodo-*o*-tolueneazo-1-amino-8-naphthol-3:6-disulphonic acid, disodium salt, 714.

C_{18} Group.

$C_{18}H_{10}O_3$ *meso*Benzanthronecarboxylic acids, 211.
$C_{18}H_{12}N_2$ 4:4′-Dicyano-$\alpha\delta$-diphenylbutadiene, 112.
$C_{18}H_{14}O_2$ 3:10-Diketo-3:4:9:10:11:12-hexahydro-1:2-benzanthracene, 586.
$C_{18}H_{16}O_6$ ω-Acetoxy-4-(4′-acetoxyphenoxy)acetophenone, 350.
Elliptol, 592.
$C_{18}H_{18}O_2$ 2:7-Dimethoxy-1:8-dimethylphenanthrene, 684.
$C_{18}H_{18}O_4$ γ-Phenyl-γ-benzylmethylsuccinic acid, 586.
$C_{18}H_{18}O_6$ Dihydroelliptol, 592.
$C_{18}H_{18}N_4$ 4:4′-Diamidino-$\alpha\delta$-diphenylbutadiene, dihydrochloride of, 110.
$C_{18}H_{20}O_6$ Tetrahydroelliptol, 593.
$C_{18}H_{22}N_4$ 2-(β-Diethylaminoethylamino)-5:6:2′:3′-pyridoquinoline, and its picrate, 218.
$C_{18}H_{26}O_2$ Acetyl-6-(2′:6′:6′-trimethyl*cyclo*hexenyl)-4-methylhex-4-en-1-yn-2-ol, 733.
$C_{18}H_{28}O_2$ Laurylbenzoquinone, 661.
$C_{18}H_{30}O_2$ Laurylquinol, 660.
$C_{18}H_{30}O_8$ Ethyl β-methylpentane-$\beta\delta\epsilon\epsilon$-tetracarboxylate, 208.
$C_{18}H_{31}N$ Benzyl-*n*-amylhexylamine, 403.
Benzylethylnonylamine, 403.
$C_{18}H_{24}O_3$ Ethyl 5-keto-3-methyl-3-*n*-amyldecoate, 496.
d-Oxidostearic acid, 390.
$C_{18}H_{34}O_8$ Bis-α-hydroxy-ω-carboxyoctyl peroxide, 219.
$C_{18}H_{36}O_4$ 9:10-Dihydroxystearic acid, 389.
$C_{18}H_{38}O_4$ Bis-α-hydroxynonyl peroxide, 220.

18 III

$C_{18}H_{12}O_2S_2$ 6-Ethoxythioindirubin, 411.
$C_{18}H_{16}O_2N_2$ 4:4′-Dicyano-$\alpha\delta$-diphenoxybutane, 114.
$C_{18}H_{16}O_6N_2$ Ethyl 1-nitrocarbazole-3:6-dicarboxylate, 503.
$C_{18}H_{17}ON_3$ 2-Benzeneazo-6-ethoxylepidine, 383.
$C_{18}H_{17}O_2N$ *iso*Butenylethinylcarbinol β-naphthylurethane, 735.
4-Methylhex-4-en-1-yn-3-ol α-naphthylurethane, 735.
2-Phenoxy-6-ethoxylepidine, 383.
4-Phenoxy-6- and -8-ethoxyquinaldines, 383.
$C_{18}H_{18}O_2N_2$ 2:3-Bisbenzamido-1-methyl*cyclo*propane, 174.
$C_{18}H_{21}O_2N$ 1-Methyl*cyclo*hexanol α-naphthylurethane, 136.
$C_{18}H_{21}O_3N_3$ *p*-*n*-Butylphenyl methyl ketone *p*-nitrophenylhydrazone, 308.
$C_{18}H_{22}O_2N_4$ 4:4′-Diamidino-$\alpha\delta$-diphenoxybutane, dihydrochloride of, 110.
$C_{18}H_{24}O_5N_2$ 5:5-Diethoxy-1-phenyl-2-methylpent-3-yn-2-ol urethane, 736.
$C_{18}H_{27}O_2N_3$ $\alpha\alpha$′-Dicyano-β-methyl-β-*n*-decylglutarimide, 495.
$C_{18}H_{29}ON_3$ 7-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-5-methylhepta-3:5-dien-2-one semicarbazone, 733.
$C_{18}H_{32}NI$ Benzyldimethylnonylammonium iodide, 403.

18 IV

$C_{18}H_{10}O_2Cl_2S_2$ 5:5′-Dichloro-7:7′-dimethylthioindigo, 412.
5:6′-Dichloro-4:4′-dimethylthioindigo, 412.
$C_{18}H_{13}ON_4Cl$ 3-Chloro-2:4-bisbenzeneazophenol, 434.
$C_{18}H_{13}ON_4Br$ 3-Bromo-2:4-bisbenzeneazophenol, 435.
$C_{18}H_{13}ON_4I$ 3-Iodo-2:4-bisbenzeneazophenol, 435.
$C_{18}H_{13}O_2NS$ 3-(6-Ethoxythionaphthen)indoleindigo, 414.
$C_{18}H_{13}O_6N_3S_2$ 4-(*p*-Nitrobenzenesulphonamido)-4′-nitrodiphenyl sulphide, 244.
$C_{18}H_{15}Cl_3AlAs$ Trichlorotriphenylarsinealuminium, 669.
$C_{18}H_{15}Cl_6AlAs_3$ Trichlorotris(phenyldichloroarsine)aluminium, 670.
$C_{18}H_{16}O_6N_2S$ 4:4′-Biscarboxyacetamidodiphenylsulphone, 43.
$C_{18}H_{19}O_3N_2S$ N^4-(6′-Ethoxy-2′-lepidyl)sulphanilamide, 758.
N^4-(Ethoxy-4′-quinaldyl)sulphanilamides, 758.

18 V

$C_{18}H_{16}O_3N_3ClS$ N^4-Acetyl-N^1-(6-chlorolepidyl)sulphanilamide, 429.

C_{19} Group.

$C_{19}H_{12}O_3$ Methyl *meso*benzanthronecarboxylates, 211.
$C_{19}H_{13}N$ 3-Phenylacridine, and its picrate, 695.
$C_{19}H_{17}N$ 7-Phenyl-1:2:3:4-tetrahydroacridine, and its picrate, 695.
$C_{19}H_{18}O_6$ Elliptol methyl ether, 592.
$C_{19}H_{19}N_3$ 7-Phenylamino-1:2:3:4-tetrahydroacridine, and its picrate, 696.

$C_{19}H_{22}O_{10}$ 5:5′-Methylenebis-2-hydroxy-3:4-dimethoxybenzoic acid, 727.
$C_{19}H_{24}N_4$ (β-Diethylaminoethylamino)methylpyridoquinolines, and their salts, 217.
$C_{19}H_{29}N_3$ α-Diethylamino-δ-amyl-lepidylamine, and its dipicrate, 427.
$C_{19}H_{30}O_3$ 5-Hydroxy-3-methyl-2-decylcoumarin, 661.
$C_{19}H_{32}O$ 8-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-3:6-dimethylocta-4:6-dien-3-ol, 733.
$C_{19}H_{32}O_6$ Ethyl 5-keto-6-acetyl-6-carbethoxy-3:3-dimethylundecoate, 493.
$C_{19}H_{38}O_2$ 1-Methyl-1-*n*-octyldecoic acid, 493.
$C_{19}H_{41}N$ Methylnonylamine, 403.

19 III

$C_{19}H_{13}O_2N$ 9-Acetamido*meso*benzanthrone, 211.
$C_{19}H_{13}O_3I$ 2-Keto-5-styryl-2:3-dihydrofuran, di-*o*-iodobenzoyl derivative, 35.
$C_{19}H_{14}ON_2$ 1-Benzamidocarbazole, 510.
$C_{19}H_{14}O_4N_2$ Phenyl *p*-nitrophenylimidocarbonate, 153.
$C_{19}H_{15}ON_3$ β-Benzoyl-αα-diphenylhydrazyl, equilibrium of, with dibenzoyltetraphenyltetrazan, 621.
$C_{19}H_{15}O_2N$ Phenyl phenylimidocarbonate, 153.
$C_{19}H_{16}N_2Cl$ *s*-Diphenyl-*p*-chlorophenylguanidine, hydrochloride of, 152.
$C_{19}H_{17}N_3S_2$ γ-Azatrimethin[2-(3-ethyldihydrobenzthiazole)][3-(2:4-benzthiazine)], 102.
$C_{19}H_{18}O_2N_2$ 4:4′-Dicyano-αε-diphenoxypentane, 114.
$C_{19}H_{19}ON$ 1-(Diphenylyl-4′-iminomethyl)*cyclo*hexan-2-one, 695.
$C_{19}H_{19}N_2I$ 2-Methylanilinovinylquinoline methiodide, 712.
$C_{19}H_{20}ON_2$ 1-(Phenylaminophenyliminomethyl)*cyclo*hexan-2-one, 696.
$C_{19}H_{20}O_5N_4$ 5-Methoxy-1:1-dimethyl-β-tetralone 2:4-dinitrophenylhydrazone, 691.
$C_{19}H_{21}O_2N$ 1:2-Dimethyl*cyclo*hexen-3-ol α-naphthylurethane, 137.
$C_{19}H_{23}O_2N$ *dl*-Ethyl-*n*-propyl carbinyl *p*-xenylurethane, 25.
$C_{19}H_{23}O_5N_3$ *p*-*n*-Amylphenyl methyl ketone *p*-nitrophenylhydrazone, 308.
$C_{19}H_{24}O_2N_4$ Diamidino-αε-diphenoxypentanes, salts of, 110.
$C_{19}H_{26}O_5N_2$ 5-Keto-3:3-dimethylundecoic acid 2:4-dinitrophenylhydrazone, 494.
$C_{19}H_{28}N_2Cl$ α-Diethylamino-δ-amyl-6-chlorolepidylamine, 429.
$C_{19}H_{39}ON$ 2-*n*-Octylundecamide, 493.

19 IV

$C_{19}H_{12}O_4N_2Cl_2$ *p*-Chlorophenyl *p*-nitrophenylimidocarbonate, 153.
$C_{19}H_{13}O_3ClS_2$ Chloro-6′-ethoxymethylthioindigos, 412.
Chloro-6′-ethoxymethylthioindirubins, 412.
$C_{19}H_{13}O_6N_2S$ Dinitro-9-*p*-toluenesulphonylcarbazoles, 510.
$C_{19}H_{14}O_2NBr$ Phenyl *p*-bromophenylimidocarbonate, 153.
$C_{19}H_{14}O_4N_2S$ Nitro-9-toluenesulphonylcarbazoles, 503, 504, 510.
$C_{19}H_{16}O_2N_2S$ 1-Amino-9-*p*-toluenesulphonylcarbazole, 510.
$C_{19}H_{19}O_4N_3S$ N^4-Acetyl-N^1-(6-methoxylepidyl)sulphanilamide, 428.
$C_{19}H_{26}ON_2Cl$ Diethyl-δ-aminoamylamine 6-chlorocinchoninamide, 429.

19 V

$C_{19}H_{14}O_2NBrS$ 3-Bromo-9-*p*-toluenesulphonylcarbazole, 510.

C_{20} Group.

$C_{20}H_{26}$ 3:4-Di-*tert.*-butylacenaphthene, 564.

20 II

$C_{20}H_{12}O_7$ Elliptonone, 593.
$C_{20}H_{14}O_3$ Ethyl *meso*benzanthronecarboxylates, 210.
$C_{20}H_{16}O_6$ Dehydrodihydroelliptones, 592.
Elliptone, reduction of, 587.
Elliptol *iso*flavone, 597.
$C_{20}H_{18}O_6$ Dehydrotetrahydroelliptone, 592.
Dihydroelliptones, 591.
$C_{20}H_{18}O_7$ Dehydrotetrahydromalaccol, 595.
Elliptol *iso*flavanonol, 597.
$C_{20}H_{18}O_8$ ω:3-Diacetoxy-4-(4′-acetoxyphenoxy)acetophenone, 350.
$C_{20}H_{20}O_5$ Dihydrodeoxyelliptones, 591.
$C_{20}H_{20}O_6$ Dihydroelliptic acid, 592.
$C_{20}H_{22}O_2$ 3:4-Di-*tert.*-butylacenaphthenequinone, 564.
$C_{20}H_{22}O_3$ 4:5-Di-*tert.*-butylnaphthalic anhydride, 564.
$C_{20}H_{22}O_6$ Tetrahydroelliptic acid, 593.
$C_{20}H_{22}O_9$ Tetrahydromalaccolic acid, 594.
$C_{20}H_{26}O_5$ Octahydrodeoxyelliptone, 591.
$C_{20}H_{28}O_7$ Ethyl ε-phenoxypentane-αββ-tricarboxylate, 423.
$C_{20}H_{28}O_{14}$ Hepta-acetyl *dl*-galactose, from 3:6-anhydro-β-methyl-*d*-galactoside, 749.
$C_{20}H_{32}O_2$ Myristylbenzoquinone, 661.
$C_{20}H_{32}O_3$ 2:5-Dimethoxylaurophenone, 660.
$C_{20}H_{34}O_2$ 2:5-Dimethoxylaurylbenzene, 660.
Myristylquinol, 660.
$C_{20}H_{34}O_8$ Ethyl octane-1:4:5:8-tetracarboxylate, 692.
$C_{20}H_{38}O_2$ Ethyl 3-methyl-3-(β-*cyclo*hexylethyl)nonoate, 495.
$C_{20}H_{38}O_3$ 5-Keto-3-methyl-3-*n*-octylundecoic acid, 494.
$C_{20}H_{40}O_2$ 2:2-Dimethylstearic acid, 492.

20 III

$C_{20}H_{16}O_2S_2$ Benzthioindirubins, 411.
$C_{20}H_{12}O_4N_4$ 5:5′-Dinitro-1:1′-azonaphthalene, 746.
$C_{20}H_{12}NCl$ 4′-Chloro-2′-methyl-1′-aza-3:4-benzpyrene, 377.
$C_{20}H_{12}N_2Cl_2$ 4:4′-Dichloro-1:1′-azonaphthalene, 47.
Dichloroazonaphthalenes, 746.
$C_{20}H_{13}ON$ 4′-Hydroxy-2′-methyl-1′-aza-3:4-benzpyrene, 377.
$C_{20}H_{15}O_2N$ Phenylethinylcarbinol β-naphthylurethane, 734.
$C_{20}H_{16}OS$ α-Benzoylbenzhydrylthiol, 94.
$C_{20}H_{16}O_4S_2$ 6:6′-Diethoxythioindirubin, 412.
$C_{20}H_{16}O_7N_4$ 3-Hydroxy-4-(4′-hydroxyphenoxy)acetophenone 2:4-dinitrophenylhydrazone, 351.
$C_{20}H_{17}O_2N$ Phenyl *p*-tolylimidocarbonate, 153.
$C_{20}H_{17}NS$ Thiobenzobenzylanilide, 641.
$C_{20}H_{18}O_3S$ *p*-Tolylbenzhydrylsulphone, 610.
$C_{20}H_{18}N_2S_2$ Trimethin[2-(3-ethyldihydrobenzthiazole)][3-(2:4-benzthiazine)], 101.
$C_{20}H_{20}O_2N_2$ 4:4′-Dicyano-αζ-diphenoxyhexane, 114.
$C_{20}H_{22}N_2I$ 2-(1:3-Dimethylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine iodide, 712.
$C_{20}H_{23}O_2N$ 4:5-Di-*tert.*-butylnaphthalimide, 564.
$C_{20}H_{23}O_2N$ 4:5-Di-*tert.*-butylnaphthaloxime, 564.
$C_{20}H_{25}O_2N_3$ *p*-*n*-Hexylphenyl methyl ketone *p*-nitrophenylhydrazone, 308.
$C_{20}H_{26}O_2N_4$ 4:4′-Diamidino-αζ-diphenoxyhexane, dihydrochloride of, 110.
$C_{20}H_{26}O_4N_4$ 3-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-1-methylcrotonaldehyde 2:4-dinitrophenylhydrazone, 732.
$C_{20}H_{28}O_2N_2$ 2′:2′:6′-Trimethylpiperidinomethyl-6-methoxy-4-quinolylcarbinol, and its dipicrate, 404.
$C_{20}H_{30}O_2N_2$ Ethylhexylaminomethyl-6-methoxy-4-quinolylcarbinol, and its dipicrate, 404.
$C_{20}H_{30}O_6N_4$ 5-Keto-3:3-dimethyl-lauric acid 2:4-dinitrophenylhydrazone, 495.
$C_{20}H_{31}ON_3$ α-Diethylamino-δ-amyl-6-methoxylepidylamine, 428.
$C_{20}H_{36}NI$ Benzyldiethylnonylammonium iodide, 403.

20 IV

$C_{20}H_{11}O_2NS$ Benzthionaphthenindole-indigos, 414.
$C_{20}H_{14}O_4N_2S$ 4-Amino-4′-phthalimidodiphenylsulphone, 44.
$C_{20}H_{15}O_2N_2Cl$ 3-Chlorodibenzaminophenols, 435.
$C_{20}H_{16}O_4N_2S$ N^1N^4-Dibenzoylsulphanilamide, 241.
$C_{20}H_{16}O_5N_2S$ 4-Amino-4′-*o*-carboxybenzamidodiphenylsulphone, 45.
$C_{20}H_{16}O_6N_2S$ 4:4′-Bis-succinimidodiphenylsulphone, 44.
$C_{20}H_{18}ON_2S$ Trimethin[2-(3-ethyldihydrobenoxazole)][3-(2:4-benzthiazine)], 101.
$C_{20}H_{18}N_2SSe$ Trimethin[2-(3-ethyldihydrobenzselenazole)][3-(2:4-benzthiazine)], 102.
$C_{20}H_{20}O_8N_2S$ 4:4′-Biscarbethoxyformamidodiphenylsulphone, 43.
4:4′-Bis-β-carboxypropionamidodiphenylsulphone, 44.
$C_{20}H_{24}O_3N_2S$ Sulphanilylmyristamide, 241.

C_{21} Group.

$C_{21}H_{14}N_2$ 4:4′-Dicyanotriphenylmethane, 111.
$C_{21}H_{14}N_4$ 4:4′-Dicyanobenzophenone phenylhydrazone, 111.
$C_{21}H_{16}O_3$ 4-Keto-1-phenyl-1:2:3:4-tetrahydro-2-phenanthroic acid, 587.
$C_{21}H_{16}O_4$ γ-Phenyl-γ-naphthylitaconic acid, 587.
$C_{21}H_{18}O_3$ *p*-Methoxybenzhydryl benzoate, 609.
$C_{21}H_{18}O_4$ γ-Phenyl-γ-naphthylmethylsuccinic acid, 587.
$C_{21}H_{20}O_4$ γ-Phenyl-γ-(6-tetralyl)itaconic acid, 587.
$C_{21}H_{20}O_{10}$ 6:6′-Methylenebis-4-hydroxy-3:5-dimethoxyphthalide, 727.
$C_{21}H_{30}N_4$ 4:4′-Diamidinotriphenylmethane, dihydrochloride of, 110.
$C_{21}H_{22}O_9$ Methyl dihydroelliptate, 592.
$C_{21}H_{24}O_8$ Methyl tetrahydroelliptate, 594.
$C_{21}H_{24}O_9$ Methyl tetrahydromalaccolate, 594.
$C_{21}H_{16}O_4$ *d*-5-Hydroxy-5′-methyl-7-*n*-amyl-3:4-*cyclo*hexenocoumarin acetate, 187.
$C_{21}H_{25}N_4$ 2-(δ-Diethylamino-α-methylbutylamino-5:6:2′:3′-pyridoquinoline, and its picrate, 218.
$C_{21}H_{30}O_2$ *d*-Tetrahydrocannabinol, 188.
$C_{21}H_{30}O_3$ Pyrethrin I, structure of, 671.
$C_{21}H_{32}O_2$ γ-Phenyl-α-methyl-α-*n*-decylbutyrolactones, 496.
$C_{21}H_{32}O_3$ 2-Phenacyl-2-methyl-lauric acid, 496.
$C_{21}H_{34}O_4$ 2:4:5-Trimethoxylaurophenone, 660.
$C_{21}H_{36}O_2$ 4-αα-Dimethylundecylveratrole, 493.

21 III

$C_{21}H_{13}ON_3$ *N*-Benzoyl-4:4′-dicyanodiphenylamine, 116.
N-4-Cyanophenylbenzimino-4′-cyanophenyl ether, 116.
$C_{21}H_{16}O_3S$ Desyl thiobenzoate, 93.
$C_{21}H_{18}O_5N_4$ 4-(4′-Methoxyphenoxy)acetophenone 2:4-dinitrophenylhydrazone, 351.
$C_{21}H_{19}ON_5$ 4:4′-Diamidino-*N*-benzoyldiphenylamine, 111, 116.
$C_{21}H_{19}O_2N$ *p*-Tolyl phenylimidocarbonate, 153.
$C_{21}H_{20}O_3S$ *p*-Tolyl-*p*-methoxybenzhydrylsulphone, 610.
$C_{21}H_{22}O_2N_2$ 4:4′-Dicyano-αη-diphenoxyheptane, 114.
$C_{21}H_{32}O_3N_2$ 4:7-Dimethyl-2-*iso*propyl-5-indanol 3:5-dinitrobenzoate, 561.
$C_{21}H_{33}O_2N$ 4-Ethyloct-4-en-1-yn-3-ol α-naphthylurethane, 735.
$C_{21}H_{34}O_2N_2$ *NN′*-Bis-(α-phenylbutyryl)carbamide, 223.
$C_{21}H_{45}O_2N$ 4:5-Di-*tert.*-butylnaphthal-*N*-methylimide, 564.

$C_{21}H_{27}O_2N_3$ *p-n*-Heptylphenyl methyl ketone *p*-nitrophenylhydrazone, 308.
$C_{21}H_{28}O_2N_4$ 4:4′-Diamidino-$\alpha\eta$-diphenoxyheptane, and its hydrochloride, 110.
$C_{21}H_{29}ON_3$ 3-(2′:6′:6′-Trimethyl*cyclo*hexenyl)-1-methylcrotonaldehyde phenylsemicarbazone, 732.
$C_{21}H_{32}O_2N_2$ Propylhexylaminomethyl-6-methoxy-4-quinolylcarbinol, and its dipicrate, 404.

21 IV

$C_{21}H_{11}O_2ClS_2$ 5′-Chloro-7′-methylbenzthioindigos, 412.
5-Chloro-7-methyl-5′:6′-benzthioindirubin, 413.
$C_{21}H_{13}O_2N_2Cl$ 6-Chloro-4-(4′-benzoyloxyphenyl)cinnoline, 357.
$C_{21}H_{16}ONBr$ α-Phenyl-α-(5-bromo-2-benzamidophenyl)ethylene, 355.
$C_{21}H_{17}O_4NS$ α-(*p*-Nitrotriphenylmethylthio)acetic acid, 92.
$C_{21}H_{18}O_2NBr$ Phenyl-(5-bromo-2-benzamidophenyl)methylcarbinol, 355.
$C_{21}H_{18}O_2N_2S$ 1-Acetamido-9-*p*-toluenesulphonylcarbazole, 510.
$C_{21}H_{20}ON_2I$ 2-(1:3-Dimethylquinoxaline)-2-(1-methylbenoxazole)trimethincyanine iodide, 713.
$C_{21}H_{22}N_2IS_2$ [2-(3-Ethylbenzthiazole)][3-(4-ethyl-2:4-benzthiazine)]-γ-azatrimethincyanine iodide, 102.
$C_{21}H_{25}O_4N_2S$ 2-(1:3-Dimethylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine methosulphate, 712.

C_{22} Group.

$C_{22}H_{16}O_5$ *p*-Methoxybenzhydryl hydrogen phthalates, 607.
$C_{22}H_{20}O_7$ *O*-Acetyldehydrotetrahydroelliptone, 594.
$C_{22}H_{20}N_2$ 3:4:7:8:9:10-Hexahydronaphtha(1:2-5:6)-bis-(2:3)-indole, 693.
$C_{22}H_{22}O_5$ Ethyl elliptate, 592.
$C_{22}H_{24}O_6$ *iso*Derritol methyl ether, 597.
$C_{22}H_{24}O_5$ Ethyl dihydroelliptate, 592.
$C_{22}H_{26}N_4$ *trans*-Decalin-1:5-dione diphenylhydrazone, 693.
$C_{22}H_{30}O_5$ Pyrethrin II, structure of, 671.
$C_{22}H_{30}N_4$ 4:4′-Di-*N*-diethylamidinodiphenyl, dihydrochloride of, 110.
(δ-Diethylamino-α-methylbutylamino)methylpyridoquinolines, and their picrates, 217.
$C_{22}H_{36}O_2$ Palmitylbenzoquinone, 661.
$C_{22}H_{36}O_3$ 2:5-Diethoxylaurophenone, 660.
2:5-Dimethoxymyristophenone, 660.
1-2′:4′:5′-Trimethoxyphenyl-1-methyl-Δ^1-duodecene, 661.
$C_{22}H_{38}O_2$ 2:5-Diethoxylaurylbenzene, 660.
2:5-Dimethoxymyristylbenzene, 660.
Palmitylquinol, 660.
$C_{22}H_{42}O_2$ Brassidic acid, preparation of, 481.
Erucic acid, preparation and oxidation of, 477.
$C_{22}H_{42}O_3$ Methyl 5-keto-3-methyl-3-*n*-octyl-laurate, 495.
$C_{22}H_{42}O_4$ Hydroxyketobehenic acid, 481.

22 III

$C_{22}H_{14}O_3S_2$ Ethoxybenzthioindirubins, 412, 413.
$C_{22}H_{16}O_2N_2$ 1:4-Di-(4′-cyanobenzyloxy)benzene, 114.
ωω′-Di-(4′-cyanophenoxy)-*p*-xylene, 114.
$C_{22}H_{16}N_2Cl$ *NN*-Diphenyl-6-chloro-4-quinolylamidine, 431.
$C_{22}H_{18}ON_2$ 9′-Keto-3′(or 4′)-*tert.*-butyl-8′-azaphenalino(7′:8′:2:3)-ψ-indole, 564.
$C_{22}H_{18}O_2N_2$ 4:4′-Dimethoxy-1:1′-azonaphthalene, 47.
$C_{22}H_{18}O_3S$ α-(Benzoylbenzhydrylthio)acetic acid, 94.
$C_{22}H_{19}O_2N$ Ethyl β-3-pyrenylaminocrotonate, 377.
$C_{22}H_{20}O_2N_2$ 4-*tert.*-Butylnaphthalphenylhydrazide, 564.
$C_{22}H_{21}O_2N$ *p*-Tolyl *o*-tolylimidocarbonate, 153.
$C_{22}H_{22}O_2N_4$ 1:4-Di-(4′-amidinobenzyloxy)benzene, dihydrochloride of, 111.
ωω′-Di-(4′-amidinophenoxy)xylene, dihydrochloride of, 110.
$C_{22}H_{22}O_2N_2$ 2:2′-Diketodi*cyclo*pentyl bis-2:4-dinitrophenylhydrazone, 692.
$C_{22}H_{26}O_4N_4$ 1-Keto-3-*cyclo*hexenyl-Δ^2-octahydrophenanthrene 2:4-dinitrophenylhydrazone, 395.
$C_{22}H_{28}O_7N_4$ 12-Acetyl-9-ketotetradecahydrophenanthrene 2:4-dinitrophenylhydrazones, 394.
$C_{22}H_{29}O_2N_3$ *p-n*-Octylphenyl methyl ketone *p*-nitrophenylhydrazone, 308.
$C_{22}H_{34}O_3N_2$ Butylhexylaminomethyl-6-methoxy-4-quinolylcarbinol, and its dipicrate, 404.
Methylnonylaminomethyl-6-methoxy-4-quinolylcarbinol, and its dipicrate, 404.

22 IV

$C_{22}H_{14}ON_2S_2$ Bis-(α-naphthylthiocarbimide) oxide, 375.
$C_{22}H_{23}N_2IS_2$ [2-(3-Ethylbenzthiazole)][3-(4-ethyl-2:4-benzthiazine)]trimethincyanine iodide, 102.

C_{23} Group.

$C_{23}H_{20}O_4$ Dimethyl γ-phenyl-γ-naphthylitaconate, 587.
$C_{23}H_{22}O_6$ Derritol *iso*flavones, 597.
$C_{23}H_{24}O_6$ Dihydroderritol *iso*flavone, 597.
$C_{23}H_{24}O_{10}$ 6:6′-Methylenebis-3:4:5-trimethoxyphthalide, 726.
$C_{23}H_{26}O_5$ *l*-Dihydrodeoxy*iso*rotenone, 593.
$C_{23}H_{38}O_2$ 1-2′:5′-Dimethoxyphenyl-1-methyl-Δ^1-tetradecene, 661.
5-Hydroxy-3-methyl-2-tetradecylcoumaran, 661.
5-Methoxy-2-tetradecylcoumarin, 661.

$C_{23}H_{38}O_3$ 4-Methoxyphenyl palmitate, 660.
$C_{23}H_{44}O_2$ Ethyl 2-methyl-2-(*β-cyclo*hexylethyl)laurate, 496.
$C_{23}H_{44}O_3$ Methyl oxidobrassidate, 482.
Methyl oxidoerucate, 482.
$C_{23}H_{45}N$ 2-Methyl-2-*n*-decyl-lauronitrile, 493.
$C_{23}H_{46}O_4$ Methyl 13:14-dihydroxybehenate, 482.

23 III

$C_{23}H_{20}O_3S$ *β*-(Benzoylbenzhydrylthio)propionic acid, 94.
$C_{23}H_{23}N_4I$ Bis-2-(1:3-dimethylquinoxaline)trimethincyanine iodide, 713.
$C_{23}H_{45}O_4N_3$ Hydroxyketobehenic acid semicarbazone, 481.

23 IV

$C_{23}H_{29}O_4N_3S$ 2-(3-Methyl-1-ethylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine ethosulphate, 712.

C_{24} Group.

$C_{24}H_{12}O_2$ 1″-Ketoindeno-2″:3″:2′:1′-benzanthrone, 628.
$C_{24}H_{14}O$ Indeno-2″:3″:2′:1′-benzanthrone, 626.
$C_{24}H_{14}O_3$ 1′-Phenylbenzanthrone-2′-carboxylic acid, 628.
$C_{24}H_{16}O$ Dihydroindeno-2″:3″:2′:1′-benzanthrone, 627.
$C_{24}H_{22}O_2$ *β*-Hydroxy-*β*-methyltrimethylene-*αγ*-bis-2-naphthyl ether, 171.
$C_{24}H_{22}O_3$ *O*-Diacetyldehydrotetrahydromalaccol, 595.
$C_{24}H_{24}O_3$ Ethyl acetylelliptate, 592.
$C_{24}H_{40}O_2$ 1-2′:5′-Dimethoxyphenyl-Δ^1-hexadecene, 661.
Stearylbenzoquinone, 661.
$C_{24}H_{40}O_3$ 2:5-Diethoxymyristophenone, 660.
2:5-Dimethoxypalmitophenone, 660.
$C_{24}H_{42}O_2$ 2:5-Diethoxymyristylbenzene, 660.
2:5-Dimethoxypalmitylbenzene, 660.
Stearylquinol, 660.
$C_{24}H_{42}O_3$ 1-Hydroxy-1-2′:5′-dimethoxyphenylhexadecane, 661.

24 III

$C_{24}H_{12}O_2S_2$ Dibenzthioindigos, 413.
Dibenzthioindirubins, 413.
$C_{24}H_{18}O_2S$ 3′-*tert.*-Butyl-1:7′-thionaphthenacenaphthenylindigo, 564.
$C_{24}H_{20}N_2S_2$ Trimethin[2-(3-ethyldihydro-4:5-benzbenzthiazole)][3-(2:4-benzthiazine)], 102.
$C_{24}H_{23}N_2I$ 2-(1-Phenylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine iodide, 713.
$C_{24}H_{25}N_2I$ 2-(1:3-Dimethylquinoxaline)-2-(1:3:3-trimethylindoline)trimethincyanine iodide, 712.
$C_{24}H_{28}O_2N_2$ 4:4′-Dicyano-*ακ*-diphenoxydecane, 114.

24 IV

$C_{24}H_{20}ON_2S$ Trimethin[2-(3-ethyldihydro-6:7-benzbenzoxazole)][3-(2:4-benzthiazine)], 101.
$C_{24}H_{24}O_2N_2S$ 2-[*p*-(2′-1′:2′:3′:4′-Tetrahydro*iso*quinolyl)benzenesulphonyl]-1:2:3:4-tetrahydro*iso*quinoline, 739.
$C_{24}H_{36}O_2N_2S$ Sulphanilylchaulmoogramide, 241.
$C_{24}H_{40}O_2N_2S$ N^1-Dihydrochaulmoogrylsulphanilamide, 243.
Dihydrosulphanilylchaulmoogramide, 241.

C_{25} Group.

$C_{25}H_{42}O_2$ 1-2′:5′-Dimethoxyphenyl-1-methyl-Δ^1-hexadecene, 661.
5-Hydroxy-3-methyl-2-hexadecylcoumaran, 661.
$C_{25}H_{42}O_3$ 4-Methoxyphenyl stearate, 660.
$C_{25}H_{45}N$ Benzyldinonylamine, 403.

25 III

$C_{25}H_{22}IAs$ Triphenyl-*p*-tolylarsonium iodide, 669.
$C_{25}H_{24}N_2Cl$ 2-(1-Phenyl-3-methylquinoxaline)-1-(4-dimethylaminobenzene)dimethincyanine chloride, 713.

25 IV

$C_{25}H_{17}O_4ClS_2$ 6′-Chloro-4′-methylbenzthioindigos, 412.
$C_{25}H_{20}NSP$ Tetraphenylphosphorium thiocyanate, 670.
$C_{25}H_{20}NSAs$ Tetraphenylarsonium thiocyanate, 669.

C_{26} Group.

$C_{26}H_{16}O_2$ Dixanthylen, reaction of, with sulphur, 272.
$C_{26}H_{16}S_2$ Dithioxanthylen, 274.
$C_{26}H_{18}O_3$ Ethyl 1′-phenylbenzanthrone-2′-carboxylate, 628.
$C_{26}H_{32}N_4$ 4:4′-Di-*N*-phenylamidinodiphenyl, dihydrochloride of, 110.
$C_{26}H_{44}O_3$ 2:5-Dimethoxystearophenone, 660.

$C_{26}H_{46}O_3$ 2:5-Diethoxypalmitylbenzene, 660.
2:5-Dimethoxystearylbenzene, 660.
$C_{36}H_{62}O_2$ 5-Methyl-2-*n*-nonyl-5-*n*-decyl*cyclo*hexane-1:3-dione, 496.

26 III

$C_{26}H_{16}O_4Cl_2$ 2-Keto-5-styryl-2:3-dihydrofuran, di-*o*-chlorobenzoyl derivative, 35.
$C_{24}H_{20}OS$ Phenyl α-benzoylbenzhydryl sulphide, 95.
$C_{26}H_{24}IAs$ Diphenyldi-*p*-tolylarsonium iodide, 669.
$C_{26}H_{26}ON_2$ 9′-Keto-3′:4′-di-*tert.*-butyl-8′-azaphenalino(7′:8′:2:3)-ψ-indole, 564.
$C_{26}H_{26}O_5N_4$ 3:4-Di-*tert.*-butylacenaphthenequinone 2:4-dinitrophenylhydrazone, 565.
$C_{26}H_{27}O_3N_3$ 3:4-Di-*tert.*-butylacenaphthenequinone *p*-nitrophenylhydrazone, 565.
$C_{26}H_{28}O_2N_2$ 4:5-Di-*tert.*-butylnaphthalphenylhydrazide, 564.
$C_{26}H_{32}O_2N_2$ 2:7-Dihydroxy-1:8-bispiperidinomethylphenanthrene, 684.
$C_{26}H_{49}ON$ 2-Keto-1:3-dimethyl-3:5-di-*n*-decyl-2:3-dihydropyrrole, 495.

26 IV

$C_{26}H_{18}O_8N_4S$ 4:4′-Bis-(*p*-nitrobenzamido)diphenylsulphone, 242.
Diphenylsulphone-4:4′-bisazosalicylic acid, 244.
$C_{26}H_{20}O_3N_2S$ 1-Benzamido-9-*p*-toluenesulphonylcarbazole, 510.
$C_{26}H_{22}O_4N_2S_2$ 1-*p*-Toluenesulphonamido-9-*p*-toluenesulphonylcarbazole, 510.
$C_{26}H_{22}NSAs$ Triphenyl-*p*-tolylarsonium thiocyanate, 669.

C_{27} Group.

$C_{27}H_{24}O_3$ Robustic acid, and its salts, 182.
$C_{27}H_{26}O_3$ Dihydrorobustic acid, 182.
$C_{27}H_{46}O_2$ 1-2′:5′-Dimethoxyphenyl-1-methyl-Δ^1-octadecene, 661.

27 III

$C_{27}H_{20}O_2S$ α-Benzoylbenzhydryl thiobenzoate, 94.
$C_{27}H_{26}IAs$ Phenyltri-*p*-tolylarsonium iodide, 669.
$C_{27}H_{41}ON$ Solasodiene, 10.
$C_{27}H_{43}O_3N$ Solasodine nitrite, 9.
$C_{27}H_{43}O_2N$ Solasodine, 8.
Solauricidine, and its salts, 14.
$C_{27}H_{45}O_2N$ Dihydrosolasodine, 9.
$C_{27}H_{47}ON$ Hexahydrosolasodiene, 10.

27 IV

$C_{27}H_{18}O_4NCl$ 5-Chloro-2-benzamido-4′-benzoyloxybenzophenone, 355.

C_{28} Group.

$C_{28}H_{18}O_4$ 2:7-Dibenzoyloxyphenanthrene, 686.
$C_{28}H_{20}O_4$ 2:7-Dibenzoyloxy-9:10-dihydrophenanthrene, 687.
$C_{28}H_{26}O_3$ Methyl robustate, 182.
$C_{28}H_{28}N_6$ αβ-Bis-(4-phenylbenzamidrazino)ethylene, and its dihydrochloride, 111.
$C_{28}H_{28}O_3$ Methyl dihydrorobustate, 182.
$C_{29}H_{54}O_2$ Ethyl 5-keto-3-methyl-3-*n*-decylpentadecoate, 496.
$C_{29}H_{34}O_4$ *p*-Phenylphenacyl β-(2-acetyl-4-*iso*propyl*cyclo*pentyl)butyrate, 562.
$C_{29}H_{48}O$ ωω-Di-*n*-decylacetophenone, 493.
$C_{29}H_{50}O_2$ 2:5-Diethoxystearylbenzene, 660.

28 III

$C_{28}H_{22}O_2S$ Didesyl sulphide, 93.
$C_{28}H_{26}O_2S$ 3′:4′-Di-*tert.*-butyl-1:7′-thionaphthenacenaphthenylindigo, 565.
$C_{28}H_{28}N_2I$ 2-(1-Phenylquinoxaline)-2-(1:3:3-trimethylindoline)trimethincyanine iodide, 713.
$C_{28}H_{28}IP$ Tetratolylphosphonium iodides, 670.
$C_{28}H_{40}O_6N_4$ 2:5-Diethoxylaurophenone 2:4-dinitrophenylhydrazone, 660.

28 IV

$C_{28}H_{16}O_4N_2S$ 4:4′-Bisphthalimidodiphenylsulphone, 44.
$C_{28}H_{20}O_3NCl$ α-(5-Chloro-2-benzamidophenyl)-α-(4′-benzoyloxyphenyl)ethylene, 356.
$C_{28}H_{20}O_3NCl$ 5-Chloro-2-benzamido-2′-benzoyloxy-5′-methylbenzophenone, 357.
$C_{28}H_{20}O_8N_2S$ 4:4′-Bis-*o*-carboxybenzamidodiphenylsulphone, 45.
$C_{28}H_{28}NSAs$ Phenyltri-*p*-tolylarsonium thiocyanate, 669.
$C_{28}H_{36}O_8N_2S$ 4:4′-Bis-δ-carbethoxyvaleramidodiphenylsulphone, 44.

C_{29} Group.

$C_{29}H_{46}O_3$ Triketone, from oleanolic acid, 743.
$C_{29}H_{42}O_3$ Diketo-dehydro-acid, from deoxoglycyrrhetic acid, 743.
$C_{29}H_{44}O$ Oleadienone II, 539.
$C_{29}H_{44}O_2$ Norsiaresinodione, 543.

$C_{29}H_{46}O$ Fucostadienone, 392.
Norechinocystadienol, 539.
Norsiaresinone, 543.
Oleadienols, 539.
$C_{29}H_{48}O$ Dihydronorsiaresinol, 544.

26 III

$C_{29}H_{42}ON_2$ Pyridazine derivative from oleanolic acid, 743.
$C_{29}H_{45}O_2N$ Acetylsolasodine, 8.
$C_{29}H_{47}ON$ Fucostadienone oxime, 393.
Stigmastadienone oxime, 393.

C_{30} Group.

$C_{30}H_{22}$ 1:2:4:5-Tetraphenylbenzene, preparation of, 585.

30 II

$C_{30}H_{20}O_2$ Diflavylen, reaction of, with sulphur, 272.
$C_{30}H_{20}S_2$ Dithioflavylen, 273.
$C_{30}H_{24}Cl_2$ $a\zeta$-Dichloro-$a\gamma\delta\zeta$-tetraphenyl-$\Delta^{a\epsilon}$-hexadiene, 585.
$C_{30}H_{32}O_6$ Cannabinol *p*-carboxymethoxybenzoate, 630.
$C_{30}H_{46}O_2$ Breienedione, 201.
Maniladione, 203.
$C_{30}H_{46}O_3$ Dehydrodeoxoglycyrrhetic acid, 539.
Dehydro-oleanolic acid, 539.
$C_{30}H_{46}O_4$ Glycyrrhetic acid, structure of, 535.
$C_{30}H_{48}O_2$ Breieneonols, 202.
Deoxydeoxoglycyrrhetic acid, 538.
Elemanic acids, 549, 550.
$C_{30}H_{48}O_3$ Breienediolone, 202.
Dihydro-β-elemonic acid, 550.
Oleanolic acid, structure of, 741.
$C_{30}H_{48}O_4$ Siaresinolic acid, 540.
$C_{30}H_{48}O_6$ 2:4:5-Triacetoxystearylbenzene, 661.
$C_{30}H_{50}O_2$ Dihydro-α-elemanic acid, 549.
Dihydro-β-elemanic acid, 550.
$C_{30}H_{54}O_2$ Dihydroxydihydrosqualene, 121.

30 III

$C_{30}H_{30}O_2S$ 5-Ethoxy-3′:4′-di-*tert.*-butyl-1:7′-thionaphthenacenaphthenylindigo, 565.
$C_{30}H_{44}O_6N_4$ 2:5-Diethoxymyristophenol 2:4-dinitrophenylhydrazone, 660.
$C_{30}H_{47}O_2N$ Maniladione oxime, 203.
$C_{30}H_{49}ON_3$ Fucostadienone semicarbazone, 393.
$C_{30}H_{49}O_3N$ Dihydro-α-elemonic acid oxime, 549.

30 IV

$C_{30}H_{22}O_7N_2As$ Tetraphenylarsonium picrate, 669.
$C_{30}H_{40}O_6N_2S$ 4:4′-Bis-η-carboxyoctamidodiphenylsulphone, 44.

C_{31} Group.

$C_{31}H_{25}N_3$ Pentaphenylguanidine, and its hydrochloride, 152.
$C_{31}H_{48}O_4$ Methyl α- and β-siaresinonates, 543.
$C_{31}H_{48}O_2$ Norechinocystadienol acetate, 539.
$C_{31}H_{48}O_3$ Methyl dehydrodeoxoglycyrrhetate, 539.
Methyl β-deoxosiaresinonate, 543.
$C_{31}H_{50}O_2$ Methyl β-boswellanate, 41.
Methyl deoxydeoxoglycyrrhetate, 538.
Methyl elemanates, 549.
$C_{31}H_{50}O_3$ Methyl dihydro-α-elemonate, 549.
Methyl dihydro-β-elemonate, 550.
Methyl 21-ketodihydro-oleananate, 543.
$C_{31}H_{52}O$ Amyrin methyl ethers, 202.
$C_{31}H_{52}O_2$ Methyl dihydrobetulanate, 41.
Methyl dihydro-β-elemanate, 550.

31 III

$C_{31}H_{31}O_2N_2$ 2-(1-Phenyl-3-methylquinoxaline)-2-(1:3:3-trimethylindoline)trimethincyanine acetate, 713.

C_{32} Group.

$C_{32}H_{27}N_3$ *s*-Tetraphenyltolylguanidines, 152.
$C_{32}H_{34}N_4$ 3:4-Di-*tert.*-butylacenaphthenequinone diphenylhydrazone, 564.
$C_{32}H_{50}O_2$ Breieneonol acetates, 202.

32 III

$C_{32}H_{30}O_6N_6$ 3:4-Di-*tert.*-butylacenaphthenequinone bis-2:4-dinitrophenylhydrazone, 565.
$C_{32}H_{48}O_6N_4$ 2:5-Diethoxypalmitophenone 2:4-dinitrophenylhydrazone, 660.

32 IV

$C_{32}H_{22}O_4N_4S$ Diphenylsulphone-4:4′-bisazo-β-naphthol, 243.
$C_{32}H_{36}O_6N_2S$ 4:4′-Biscamphorimidodiphenylsulphone, 45.
$C_{32}H_{44}O_8N_2S$ 4:4′-Bis-η-carbomethoxyoctamidodiphenylsulphone, 44.

C_{33} Group.

$C_{33}H_{46}O_6$ Diketo-dehydro-ester, from deoxoglycyrrhetic acid, 743.
Diketo-dehydro-ester, from oleanolic acid, 743.
$C_{33}H_{50}O_4$ Methyl acetyldehydrodeoxoglycyrrhetate, 539.
dl-Tetrahydrocannabinol *l*-menthoxyacetate, 188.
$C_{33}H_{50}O_5$ Methyl acetyl-21-keto-oleanolate, 543.
$C_{33}H_{52}O_5$ Methyl acetylsiaresinolate, 543.
$C_{33}H_{54}O_4$ Methyl acetyldihydro-α-elemolate, 549.

33 III

$C_{33}H_{27}N_4Cl$ Bis-2-(1-phenyl-3-methylquinoxaline)trimethincyanine chloride, 713.
$C_{33}H_{48}O_5Br_2$ Methyl dibromoacetylglycyrrhetate, 744.

33 IV

$C_{33}H_{40}O_8N_4S_4$ Tetrakisbenzenesulphonmethylamidomethylmethane, 168.

C_{34} Group.

$C_{34}H_{24}S_2$ αα′α″α‴-Tetraphenyl-γγ′-dithiopyrylen, 274.
$C_{34}H_{52}O_5$ Brienediolone diacetate, 202.

34 III

$C_{34}H_{22}Cl_2S_2$ ββ′-Dichloro-αα′α″α‴-tetraphenyl-γγ′-dithiopyrylen, 274.

C_{35} Group.

$C_{35}H_{34}O_2N_4$ Bis-2-(1-phenyl-3-methylquinoxaline)trimethincyanine acetate, 713.
$C_{35}H_{50}O_4N_4$ Fucostadienone 2:4-dinitrophenylhydrazone, 393.
Stigmastadienone 2:4-dinitrophenylhydrazone, 393.
$C_{35}H_{54}O_4N_4$ Sitostenone 2:4-dinitrophenylhydrazone, 393.

C_{36} Group.

$C_{36}H_{30}O_2N_4$ Dibenzoyltetraphenyltetrazan, equilibrium of, with β-benzoyl-αα-diphenylhydrazyl, 121.

C_{37} Group.

$C_{37}H_{44}O_3S$ β-Amyrin *p*-toluenesulphonate, 202.

C_{39} Group.

$C_{39}H_{42}O_{10}$ Cannabidiol bis-*p*-carbomethoxybenzoate, 630.

C_{40} Group.

$C_{40}H_{30}O_2S_2$ Di-α-benzoylbenzhydryl disulphide, 94.

C_{42} Group.

$C_{42}H_{42}OBr_2As_2$ Tri-*o*-tolylarsine oxydibromide, 670.
$C_{42}H_{43}O_2BrAs_2$ Tri-*o*-tolylarsine hydroxy-oxybromide, 670.
$C_{42}H_{43}O_2IAs_2$ Tri-*o*-tolylarsine hydroxy-oxyiodide, 670.

C_{44} Group.

$C_{44}H_{26}O_{22}N_{10}I_2S_2$ 5:5′-Di-iodo-2:2′-disulphodiphenyl-4:4′-bis-[2″-azo-8″-amino-1‴-hydroxy-3‴:6‴-disulphonaphthalene-7″-(azo-2‴-di-iodobenzene-4‴-sulphonic acid)], octasodium salt, 716.

C_{45} Group.

$C_{45}H_{72}O_6$ Glycyrrhetic acid, structure of, 741.

45 III

$C_{45}H_{73}O_{16}N$ Solasonine, 2, 3.
Solauricine, 14, 17.

45 VI

$C_{45}H_{34}O_{20}N_{10}I_2S_4As_2$ 3:3′-Di-iododiphenylmethane-4:4′-bis-(2″-azo-7″-amino-1″-hydroxy-3″:6″-disulphonaphthalene-8″-azobenzene-4‴-arsonic acid), octapotassium salt, 715.

C_{46} Group.

$C_{46}H_{21}O_{24}N_{10}I_6S_6$ 5:5′-Di-iodo-2:2′-disulphodiphenyl-4:4′-bis-[2″-azo-8″-amino-1″-hydroxy-3″:6″-disulphonaphthalene-7″-(azo-2‴:4‴-di-iodobenzene-6‴-carboxylic acid)], trisodium salt, 716.

46 VI

$C_{46}H_{34}O_{20}N_{10}I_4S_4As$ 3:3′-Dimethyldiphenyl-4:4′-bis 2″-azo-8″-amino-1″-hydroxy-3″:6″-disulphonaphthalene-7″-(azo-2‴:6‴-di-iodobenzene-4‴-arsonic acid)], octasodium salt, 715.

C_{48} Group.

$C_{48}H_{38}O_{14}N_{10}I_2S_4$ 3:3′-Dimethyldiphenyl-4:4′-bis-[2″-azo-8″-amino-1″-hydroxy-3″:6″-disulphonaphthalene 7″-(5‴-iodo-o-azotoluene)], tetrasodium salt, 715.

C_{80} Group.

$C_{80}H_{132}O_2$ Caoutchol, 223.

ERRATA.

Vol., 1942.

Page	Line	
193	12 *	*for* "$k_1t = \frac{2{\cdot}303}{-\Delta}\log\frac{(x-a)}{a(x-\Delta)}$" *read* "$k_1t = \frac{2{\cdot}303}{a-\Delta}\log\frac{\Delta(x-a)}{a(x-\Delta)}$."
363	3 *	*for* "225°" *read* "22·5°."
364		*for the entry under* "β-Iodopentane" *substitute the following:*

0·00000	2·2350	1·5940	28·14	128	28·1
0·00664	2·2722	1·5932	28·81	127	28·2
0·01147	2·2991	1·5928	29·28	126	28·2
0·02051	2·3489	1·5916	30·15	124	28·2
0·03930	2·4534	1·5893	31·95	122	28·3
0·08770	2·7227	1·5838	36·32	115	29
0·18527	3·276	1·5730	44·44	105	31
0·41776	4·568	1·5502	60·38	93	36
1·00000	7·249	1·5020	89·09	89·1	46

518	19*	*for* "$\log_m\xi$" *read* "$\log \epsilon_m$."
579	10	*for* "carbon atom 2" *read* "carbon atom 3."
585	6—8	*substitute the following:* Nitric acid, *d* 1·42, expelled two methyl groups from 3 : 3′ : 5 : 5′-tetranitrotetramethylbenzidine; the 3 : 3′ : 5 : 5′-tetranitrodimethylbenzidine formed crystallised rapidly from hot nitrobenzene in deep yellow pyramids, m. p. 215° (decomp.) (Mertens, *Ber.*, 1886, **19**, 2125, gives red needles from phenol which decompose above 200°) (Found: N, 21·6. Calc.: N, 21·4%). Nitric acid, *d* 1·5, however, gave rise to *N* : *N*′ : 3 : 3′ : 5 : 5′-hexanitrodimethylbenzidine, which crystallised rapidly from hot nitrobenzene in bright yellow, lenticular or rhomboidal plates, m. p. 227° (decomp.), which explode in the flame (Mertens, *loc. cit.*, and Van Romburgh, *Rec. Trav. chim.*, 1886, **5**, 240, describe the compound as exploding above 220°).

* From bottom.

SYMBOLS FOR THERMODYNAMICAL AND PHYSICO-CHEMICAL QUANTITIES AND CONVENTIONS RELATING TO THEIR USE, ADOPTED AS RECOMMENDED PRACTICE BY THE CHEMICAL SOCIETY.

(Where two or more symbols separated by commas or semicolons are given for a quantity, these symbols are to be regarded as alternatives for which no preference is expressed. On the other hand, where two symbols are separated by a dotted line, the former is the first preference.)

1. To be Printed in Black Italic.

(Certain important physical constants.)

F Faraday's constant.
J Mechanical equivalent of heat.
N Avogadro's number.
R { Gas constant per mol. / Rydberg's constant.

c Velocity of light in vacuo.
e Electronic charge (charge equal and opposite in sign to that of an electron).
g Acceleration due to gravity (standard value, if variation from standard is significant).
h Planck's constant.
k Boltzmann's constant.
m Rest mass of an electron.

2. To be Printed in Ordinary Italic, when not Greek.

General Physics and Chemistry.

Length	l
mean free path of molecules	l
height	h
diameter, distance	d
diameter of molecules	σ
radius	r
Mass	m
molecular weight	M
atomic weight	A
atomic number	Z
gram-equivalent weight	Z, J
Time	t
time interval, especially half- or mean-life	τ
frequency	ν
Velocity	v; c, (u, v, w)
of ions	u (with subscript)
angular	ω
Acceleration	$f \ldots a$
due to gravity (as variable)	g
Force	F, (X, Y, Z)
Moment of inertia	I
Pressure	p, P
especially osmotic	Π
Volume	v, V
Density	$\rho \ldots d$
Compressibility	$\kappa \ldots K$

Viscosity	η
Fluidity	ϕ
Surface area	$A \ldots s$
Angle of contact	θ
Surface tension	$\gamma \ldots \sigma$
Parachor	$[P]$
Surface concentration excess	Γ
Number of mols	n
Concentration, mol fraction	N, x
in other terms	c, C
Solubility	s
Diffusion coefficient	D
Chemical equilibrium constant (products/reactants)	K
solubility product	$K_s \ldots L$
Velocity constant of chemical reaction	k
Number of molecular collisions per second	Z
Partition function	f
Efficiency, of any process	η
Wave function	ψ

Heat and Thermodynamics.

Temperature, on absolute scale, (°K)	T
on other scales	$\theta \ldots t$
Thermal conductivity	k
Energy (general symbol)	E
Work done by or on a system	$w \ldots W$
Heat entering a system	q
Specific heat	c_p and c_v
molecular heat	C_p and C
Ratio of specific heats	γ
Latent heat, per g.	l
per mol	L
Intrinsic energy	$U \ldots E$
Enthalpy, total heat, or heat content	H
Entropy	S
Free energy (Helmholtz)	$A \ldots F$
Thermodynamic potential, Gibbs function, free energy (G. N. Lewis)	G
Vapour pressure constant	i
Chemical potential	μ
Activity	a
coefficient (for molar concentration)	f
Osmotic coefficient	g
Van 't Hoff's factor	i

Electricity.

Quantity of electricity	Q
especially electrostatic charge	e
Potential (difference)	V
Volta potential	V
electrokinetic potential	ζ
especially electromotive force of voltaic cells	E
Potential gradient, in electric field	X
Electronic exit work function	ϕ

Current	I
Resistance	R
specific resistance	ρ . . . r
specific conductance	κ . . . σ
Inductance, self	L
mutual	M
Electrostatic capacity	C
Dielectric constant	ϵ
Dipole moment	μ

Electrochemistry.

Degree of electrolytic dissociation	α
Valency of an ion	z
Ionic strength	I
Equivalent conductance	Λ
equivalent ionic conductance, "mobility"	l (with subscript)
Transport number	T (with subscript) . . . n (with subscript)
Single electrode potential	e (with subscript), E (with subscript)
Electrolytic polarisation, overvoltage	η . . . π

Magnetism.

Magnetic field strength	H
flux	ϕ
permeability	μ
susceptibility—volume	κ
mass	χ
moment	M
induction	B

Optics.

Wave length	λ
Wave number	ν
Intensity of light	I
Refractive index	n (with subscript) . . . μ (with subscript)
specific refraction	r (with subscript)
molecular refraction	$[R]$ (with subscript)
Molar extinction coefficient	ϵ
Angle of (optical) rotation	α
specific rotation	$[\alpha]$
Specific magnetic rotation	ω

3. To be Printed in Roman, when not Greek.

(a) *Examples of Mathematical Constants and Operators.*

Base of natural logarithms	e
Ratio of circumference to diameter	π
Differential	d
partial	∂
Increment	Δ
very small increment	δ
Sum	Σ
Product	Π
Function	f, ϕ

(b) *Examples of single-letter abbreviations.*

*Ampère (in sub-units)	a.
Volt	v.
Ohm	Ω.
Watt	w.
Farad	f.
Henry	h.
Centigrade	c.
Fahrenheit	f.
Kelvin	k.
Ångstrom unit	a.
micron	μ.
metre	m.
gram	g.
litre	l.
Röntgen unit	r.
†Normal (concentration)	n.
†Molar (concentration)	m.

The following prefixes to abbreviations for the names of units should be used to indicate the specified multiples or sub-multiples of these units:

M	mega-	$10^{6}\times$
k	kilo-	$10^{3}\times$
d	deci-	$10^{-1}\times$
c	centi-	$10^{-2}\times$
m	milli-	$10^{-3}\times$
μ	micro-	$10^{-6}\times$

e.g., MΩ. denotes megohm; kw., kilowatt; and μg., microgram. The use of μμ. instead of mμ. to denote 10^{-7} cm., or of γ to denote microgram is deprecated.

4. Subscripts and other Modifying Signs.

(a) *Subscripts to symbols for quantities.*

I, II . . .	*especially with symbols for thermodynamic functions*, referring to different systems or different states of a system.
1, 2 . . .	
A B .	referring to molecular species A, B, etc.
i	referring to a typical ionic species i.
u	referring to an undissociated molecule.
+, −	referring to a positive or negative ion, or to a positive or negative electrode.
p, v, T	indicating constant pressure, volume, and temperature respectively.
q	indicating adiabatic conditions.
w	indicating that no work is performed.
p, c, a	*with symbol for an equilibrium constant*, indicating that it is expressed in terms of pressure, concentration, or activity.
G, V, L, X	referring to gas, vapour, liquid, and crystalline states, respectively.
f, e, s, t, d	referring to fusion, evaporation (vaporisation of liquid), sublimation, transition, and dissolution or dilution respectively.
c	referring to the critical state or indicating a critical value.
0	referring to a standard state, or indicating limiting value at infinite dilution.

* *E.g.* " ma." for " milliampère "; but " amp." is preferred for " ampère."
† Separated by a hyphen (and no full stop) from a chemical formula which follows it.

C, D, F *with symbols for optical properties*, referring to a particular wavelength.

Where a subscript has to be added to a symbol which already carries a subscript, the two subscripts may be separated by a comma or the symbol with the first subscript may be enclosed in parentheses with the second subscript outside.

(b) *Other modifying signs.*

° *as right-hand superscript to symbol (particularly to a symbol for a general thermodynamic function—see p. 5)*, referring to a standard state.

[ ] *enclosing formula of chemical substance*, indicating its molar concentration.

{ } *enclosing formula of chemical substance*, indicating its molar activity.

In crystallography it is recommended that:

Millerian indices be enclosed in parentheses, ( );
Laue indices be unenclosed;
Indices of a plane family be enclosed in braces, { };
Indices of a zone axis or line be enclosed in brackets, [ ].

Numerals attached to a symbol for a chemical element in various positions have the following meanings:

upper left mass number of atom.
lower left nuclear charge of atom.
lower right number of atoms in molecule.

e.g., ${}^{7}_{3}\mathrm{Li}$; ${}^{2}_{1}\mathrm{H}_2$ (= D_2).

ALPHABETICAL INDEX OF RECOMMENDED SYMBOLS, and single-letter abbreviations.

including all those given in the above lists except prefixes, subscripts and other modifying signs.

The name of any quantity for which a given symbol is a second preference is printed in parentheses.

A free energy—Helmholtz; atomic weight; surface area.
A. Ångstrom unit.
a activity; (acceleration).
a. ampère, in sub-units—see footnote, p. 2093.
B magnetic induction.
C concentration; electrostatic capacity.
with subscript: molecular heat capacity.
C. Centigrade.
c velocity of light in vacuo.
c velocity; concentration.
with subscript: specific heat.
D diffusion coefficient.
d diameter; distance; (density).
d differential.
∂ partial differential.
E energy; (intrinsic energy); potential difference, especially electromotive force of voltaic cells.
with subscript: single electrode potential.
e electronic charge—charge equal and opposite in sign to that of an electron.
e quantity of electricity, especially electrostatic charge.
with subscript: single electrode potential.

e base of natural logarithms.
F Faraday's constant.
F force; (free energy—Helmholtz).
F. farad; Fahrenheit.
f acceleration; activity coefficient, for molar concentration; partition function.
f function.
G thermodynamic potential, Gibbs function, free energy—G. N. Lewis.
g acceleration due to gravity, standard value.
g acceleration due to gravity, as a variable; osmotic coefficient.
g. gram.
H enthalpy, total heat, heat content; magnetic field strength.
H. henry.
h Planck's constant.
h height.
I moment of inertia; ionic strength; electric current; intensity of light.
i vapour pressure constant; van 't Hoff's factor.
J mechanical equivalent of heat.
J gram-equivalent weight.
K chemical equilibrium constant; (compressibility).
K_s solubility product.
K. Kelvin.
k Boltzmann's constant.
k thermal conductivity; velocity constant of chemical reaction.
L latent heat per mol; self inductance; (solubility product).
l latent heat per g.; length; mean free path of molecules.
with subscript: equivalent ionic conductance, " mobility ".
l. litre.
M molecular weight; mutual inductance; magnetic moment.
M. molar concentration.
m rest mass of an electron.
m mass.
m. metre.
N Avogadro's number.
N mol fraction.
N. normal concentration.
n number of mols.
with subscript: (transport number).
with subscript: refractive index.
P pressure.
[*P*] parachor.
p pressure.
Q quantity of electricity.
q heat entering a system.
R gas constant per mol; Rydberg's constant.
R electrical resistance.
[*R*] *with subscript:* molecular refraction.
r radius; (specific resistance).
with subscript: specific refraction.
r. Röntgen unit.
S entropy.
s solubility; (surface area).
T temperature, on absolute Kelvin scale.
with subscript: transport number.
t time; (temperature—not on absolute scale).
U intrinsic energy.
u velocity component.
with subscript: velocity of ions.
V volume; potential, potential difference, including Volta potential.

v. volt.
v volume; velocity; velocity component.
W (work done by or on a system).
w. watt.
w work done by or on a system; velocity component.
X force component; potential gradient in electric field.
x mol fraction.
Y force component.
Z force component; g.-equivalent weight; number of molecular collisions per second; atomic number.
z valency of an ion.

α degree of electrolytic dissociation; angle of optical rotation.
$[\alpha]$ specific optical rotation.
Γ surface concentration excess.
γ ratio of specific heats; surface tension.
Δ increment.
δ very small increment.
ϵ dielectric constant; molar extinction coefficient.
ζ electrokinetic potential.
η efficiency of any process; viscosity; electrolytic polarisation, overvoltage.
θ angle of contact; temperature—not on absolute scale.
κ compressibility; specific conductance; magnetic susceptibility—volume.
Λ equivalent conductance.
λ wave length.
μ chemical potential; dipole moment; magnetic permeability.
with subscript : (refractive index).
μ. micron.
ν frequency; wave number.
Π pressure, especially osmotic pressure.
Π product.
π (electrolytic polarisation, overvoltage).
π ratio of circumference to diameter.
ρ density; specific resistance.
Σ sum.
σ diameter of molecules; (surface tension); (specific conductance).
τ time interval, especially half or mean life.
ϕ fluidity; electronic exit work function; magnetic flux.
Φ function.
χ magnetic susceptibility—mass.
ψ wave function.
Ω. ohm.
ω angular velocity; specific magnetic rotation.

ADDITIONS TO THE LIBRARY OF THE CHEMICAL SOCIETY DURING THE YEAR 1942.

ACCUM, FREDRICK. A system of theoretical and practical chemistry. 2 vols. London 1803. (Printed on paper made of straw.) (*Reference.*)

—— A practical treatise on gaslight. London 1815. (*Reference.*)

ADAM, NEIL KENSINGTON. The physics and chemistry of surfaces. 3rd edition. London 1941. pp. xii + 436. ill.

ADVANCES IN COLLOID SCIENCE. Edited by ELMER O. KRAEMER, in collaboration with FLOYD E. BARTELL and S. S. KISTLER. Vol. I. New York 1942. pp. xii + 434. ill. (*Reference.*)

ALCHEMIST, THE. Vol. XVII. Special number. Thomas Stewart Patterson. Glasgow 1942. pp. 20. ill.

ALLEN, R. M. Photo-micrography. New York 1941. pp. viii + 365. ill.

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE. Liebig and after Liebig: a century of progress in agricultural chemistry. Edited by F. R. MOULTON. Washington 1942. pp. viii + 111. ill.

AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Cereal laboratory methods, with reference tables. 4th edition. Lincoln, Nebraska 1941. pp. xii + 264. ill.

AMERICAN SOCIETY FOR TESTING MATERIALS. Symposium on new methods for particle size determination in the subsieve range. Philadelphia 1941. pp. vi + 111. ill. (*Reference.*)

AMERICAN SOCIETY FOR TESTING MATERIALS and INTER-SOCIETY COLOR COUNCIL. Symposium on color—its specification and use in evaluating the appearance of materials. Philadelphia 1941. pp. vi + 179. ill. (*Reference.*)

AMERICAN SOCIETY OF PLANT PHYSIOLOGISTS. A symposium on the structure of protoplasm. Edited by W. SEIFRIZ. Ames 1942. pp. viii + 283.

ANNALS OF CHEMICAL MEDICINE. Edited by J. L. W. THUDICHUM. 2 vols. London 1879–81. pp. xii + 343, x + 334.

ANNUAL REVIEWS OF PETROLEUM TECHNOLOGY. *See* INSTITUTE OF PETROLEUM.

ANSLEY, A. J. Temperature control. London 1942. pp. viii + 127. ill.

ARTHUS, MAURICE. Élémens de chimie physiologique. 3rd edition. Paris [1900]. pp. x + 391.

ASSOCIATION OF CAMPHOR INDUSTRY ENGINEERS IN JAPAN. Literatures on camphor and camphor oil (1900—1939). Tokyo 1940. pp. xii + 442. (*Reference.*)

ASTON, F. W. Mass spectra and isotopes. 2nd edition. London 1942. pp. xii + 276. ill.

AUSTIN, P. C. *See* COHEN, J. B.

AUSTRALIA, COMMONWEALTH OF. *Advisory Council on Nutrition.* 5th and Final Reports. Canberra 1938. pp. 55, 165. ill. (*Reference.*)

BADGER, W. L., and BAKER, E. M. Inorganic chemical technology. 2nd edition. New York 1941. pp. xii + 237. ill.

BAHL, R. K. *See* DUNNICLIFF, H. B.

BAKER, E. M. *See* BADGER, W. L.

BARRON, HARRY. Modern synthetic rubbers. London 1942. pp. viii + 274. ill.

BARTELL, FLOYD E. *See* ADVANCES IN COLLOID SCIENCE.

BAUER, WALTER H. *See* DAVISON, ALBERT W.

BEITRÄGE ZUR WISSENSCHAFTLICHEN MEDICIN UND CHEMIE. Festschrift zu Ehren des sechszigsten Geburtstages von ERNST SALKOWSKI. Berlin 1904. pp. viii + 480.

BELL, R. P. Acid-base catalysis. Oxford 1941. pp. viii + 211. ill.

BENEDICT, R. RALPH. *See* MAXFIELD, FREDERICK A.

BENNETT, WILLIAM. The economics of coal blending in carbonizing processes. Ashton-under-Lyne 1942. pp. 50. ill.

BERKMAN, SOPHIA, and EGLOFF, GUSTAV. Emulsions and foams. New York 1941. pp. viii + 591. ill.

BERNSTEIN, JULIUS. Die Kräfte der Bewegung in der lebenden Substanz. Braunschweig 1902. pp. 28.

BERTHELOT, M. La synthèse chimique. 8th edition. Paris 1897. pp. viii + 294.

BEUTENMÜLLER, H. *See* MOHR, L.

BIERRY, H. Recherches sur les diastases qui concourent à la digestion des hydrates de carbone. Fontenay-aux-Roses 1911. pp. 282.

BIERRY, H., and RATHERY, F. Introduction à la physiologie des sucres. Paris 1935. pp. vi + 418.

BIOLOGICAL SYMPOSIA. Vol. V. Edited by HOWARD B. LEWIS. Comparative biochemistry. Intermediate metabolism of fats. Carbohydrate metabolism. Biochemistry of choline. Lancaster, Pa. 1941. pp. x + 247. ill.

BLOCH, L. Ionisation et résonance des gaz et des vapeurs. London 1925. pp. 223. ill.

BORON AGRICULTURAL BUREAU. Boron in agriculture. London 1940. pp. 36. ill.

BOURNE, G. [Editor.] Cytology and cell physiology. Oxford 1942. pp. xii + 296. ill.

BOURQUELOT, É. Les fermentations. Paris 1893. pp. iv + 204. ill.

BOWEN, E. J. The chemical aspects of light. Oxford 1942. pp. viii + 191. ill.

BOY, G. Les caractères essentials du metabolisme azoté contingent: catabolisme protéïque endogène et inanation. Lons-le-Saunier 1935. pp. x + 156.

—— Action des sels de manganèse et de zinc à concentrations toxiques sur les rendements énergétiques dans la germination. Lons-le-Saunier 1935. pp. 157 to 171.

BRIDGES, M. A., and MATTICE, M. R. Food and beverage analyses. 2nd edition. Philadelphia 1942. pp. 344.

BRIDGMAN, P. W. The nature of thermodynamics. Cambridge, Mass. 1941. pp. xii + 229.

BRITISH HARD COKE ASSOCIATION. *See* NATIONAL FEDERATION OF GAS COKE ASSOCIATIONS.

BRITISH PLASTICS YEAR BOOK, 1942. The handbook and guide to the plastics industry. Bedford 1942. pp. 464. ill. (*Reference.*)

BRITISH STANDARDS INSTITUTION. War emergency B.S. 987 and 987C: 1942. Camouflage paints. pp. 21. ill.

—— B.S. 997: 1941. Crude sperm oil. pp. 15. ill.

—— B.S. 998: 1941. Pure vacuum salt for dairy purposes. pp. 11.

—— B.S. 1011: 1942. Red lead ready mixed paints. pp. 12. ill.

—— B.S. 1013: 1942. Sanitary or disinfectant powders. pp. 8.

—— B.S. 1014: 1942. Pigments for colouring magnesium oxychloride and concrete. pp. 18.

—— War emergency B.S. 1033: 1942. Priming paint (lead base) for the protection of steel sheet. pp. 10. ill.

—— B.S. 1045: 1942. Manganese steel cylinders for atmospheric gases. pp. 12. ill.

—— War emergency B.S. 1053: 1942. Water paints and distempers for interior use. pp. 10. ill.

—— War emergency B.S. 1056: 1942. Painting of buildings in war-time. pp. 19.

—— War emergency B.S. 1057: 1942. Substitute paints: exterior finishing. pp. 9. ill.

—— B.S. 1079: 1942. Hæmoglobinometers, Haldane type. pp. 12. ill.

BRITTON, H. T. S. Hydrogen ions: their determination and importance in pure and industrial chemistry. 3rd edition. 2 vols. London 1942. pp. xix + 420; xix + 443.

BROCKLESBY, H. N. *See* CANADA. *Fisheries Research Board.*

BROGLIE, M. DE. Les rayons X. Paris 1922. pp. 164. ill.

BROUGHTON, G. *See* LEWIS, W. K.

BROWN, W. BURNS. *See* DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

BROWNE, C. A., and ZERBAN, F. W. Physical and chemical methods of sugar analysis. 3rd edition. New York 1941. pp. xiv + 1353. ill.

BRUCE, J., and HARPER, H. Practical chemistry. 5th edition. London 1941. pp. xii + 509. ill.

BRUGSCH, THEODOR, and SCHITTENHELM, ALFRED. Der Nukleinstoffwechsel und seine Störungen. (Gicht, Uratsteindiathese v.a.) Jena 1910. pp. viii + 166.

BURR, GEORGE O. *See* EVANS, HERBERT MCLEAN.

CAMERON, A. T. A textbook of biochemistry. 6th edition. London 1942. pp. viii + 376. ill.

CANADA. *Fisheries Research Board.* The chemistry and technology of marine animal oils with particular reference to those of Canada. Edited by H. N. BROCKLESBY. Ottawa 1941. pp. 442. ill.

—— *National Research Council.* Associate Committee on Trail Smelter Smoke. Effect of sulphur dioxide on vegetation. Ottawa 1939. pp. x + 447. ill.

CARLSBERG, LABORATOIRE DE. Comptes-Rendus des Travaux. Vol. XII. Copenhage 1917. (*For circulation.*)

CHEMICAL ENGINEERS' HANDBOOK. Prepared by a staff of specialists. JOHN H. PERRY, Editor. 2nd edition. New York 1941. pp. xviii + 3029. ill. (*Reference.*)

CHEMIE-INGENIEUR, DER. Vol. III. Part 3. Operationen bei normalem Druck und normaler Temperatur. Edited by A. EUCKEN. Leipzig 1939. pp. xii + 332. ill.

CHOWDHURY, R. R. Handbook of mica. Brooklyn 1941. pp. xvi + 340. ill.

CLAPPERTON, ROBERT HENDERSON, and HENDERSON, WILLIAM. Modern paper-making. Oxford 1941. pp. xii + 376. ill.

CLAYTON, WILLIAM. The theory of emulsions and their technical treatment. 4th edition. London 1942. pp. viii + 492. ill.

COHEN, J. B. Theoretical organic chemistry. 4th edition. By P. C. AUSTIN. London 1942. pp. xvi + 622. ill.

CONDENSED CHEMICAL DICTIONARY. 3rd edition. Edited by T. C. GREGORY. New York 1942. pp. 755. (*Reference.*)

COOPER-KEY, A. A primer on the storage of petroleum spirit and carbide of calcium. London 1914. pp. viii + 128.

COTTON, R. T. Insect pests of stored grain and grain products: identification, habits and methods of control. Minneapolis 1941. pp. iv + 242. ill.

DAKE, H. C. *See* DE MENT, H.

DALE, H. GORDON. *See* INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

DANIELS, FARRINGTON, MATTHEWS, J. HOWARD, and WILLIAMS, JOHN WARREN. Experimental physical chemistry. 3rd edition. New York 1941. pp. xviii + 460. ill.

DAVISON, ALBERT W., KLOOSTER, HENRY S. VAN, and BAUER, WALTER H. Laboratory manual of physical chemistry. 3rd edition. New York 1941. pp. viii + 229. ill.

DEGERING, E. F., and collaborators. An outline of organic chemistry. 4th edition. New York 1941. pp. xviii + 386.

—— The work book of fundamental organic chemistry. New York 1941. pp. 256.

—— An outline of organic nitrogen compounds. Cincinnati 1942. pp. vi + 381.

—— Fundamental organic chemistry. Cincinnati 1942. pp. x + 485. ill.

DE MENT, J. Fluorescent chemicals and their applications. With a special chapter on ultraviolet radiation sources by H. C. DAKE. Brooklyn 1942. pp. xiv + 240. ill.

DE MENT, J., and DAKE, H. C. Uranium and atomic power. Brooklyn 1941. pp. viii + 335. ill.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. The control of insects infesting dried fruits. By W. BURNS BROWN and A. E. H. HIGGINS. London 1942. pp. 23. ill.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. *Food Investigation.* Special Report No. 52. The mode of occurrence of fatty acid derivatives in living tissues: a review of present knowledge. By J. A. LOVERN. London 1942. pp. 36.

—— *Water Pollution Research.* Technical Paper No. 8. The treatment and disposal of waste waters from dairies and milk products factories. London 1941. pp. viii + 125. ill.

DESCH, C. H. Metallography. 5th edition. London 1942. pp. viii + 408. ill.

DEUTSCHE CHEMISCHE GESELLSCHAFT. Periodica Chimica. Edited by M. PFLÜCKE. Berlin 1940. pp. viii + 208. (*Reference.*)

DOBBIN, LEONARD. Occasional fragments of chemical history. Edinburgh 1942. pp. viii + 85. ill.

DOLE, MALCOLM. The glass electrode: methods, applications, and theory. New York 1941. pp. xvi + 332. ill.

DOSS, M. P. *See* TEXAS COMPANY.

DUNNICLIFF, H. B., and BAHL, R. K. A history of chemistry in the Panjab. Lahore 1927. pp. 16.

EGLOFF, GUSTAV. *See* BERKMAN, SOPHIA.

ELBEL, H. Die wissenschaftlichen Grundlagen der Beurteilung von Blutalkoholbefunden. Leipzig 1937. pp. 106. ill.

ELDRIDGE, E. F. Industrial waste treatment practice. New York 1942. pp. xii + 401. ill.

ELECTROCHEMICAL SOCIETY. Modern electroplating. New York 1942. pp. 399. ill.

ELVEHJEM, C. A. *See* WAISMAN, HARRY A.

ENDEAVOUR: a quarterly review designed to record the progress of the sciences in the service of mankind. Vol. I, etc. London 1942+. (*Reference.*)

EUCKEN, A. *See* CHEMIE-INGENIEUR, DER.

EULER, H. Grundlagen und Ergebnisse der Pflanzenchemie. 2 vols. Braunschweig 1908. pp. x + 238, x + 298.

EVANS, E. A. [Editor.] The biological action of the vitamins: a symposium. Chicago 1942. pp. x + 227. ill.

EVANS, HERBERT MCLEAN, and BURR, GEORGE O. The antisterility vitamine fat soluble E. (*Mem. Univ. California*, 8.) Berkeley 1927. pp. 176. ill.

FELL, ALFRED. The early iron industry of Furness and district: an historical and descriptive account from earliest times to the end of the 18th century, with an account of Furness ironmasters in Scotland, 1726—1800. Ulverston 1908. pp. xviii + 464. ill. (*Reference.*)

FIESER, LOUIS F. Experiments in organic chemistry. 2nd edition. New York 1941. pp. xii + 488. ill.

FINDLAY, ALEXANDER. Practical physical chemistry. 7th edition. London 1941. pp. x + 335. ill.

FITZPATRICK, FREDERICK L. The control of organisms. New York 1940. pp. xiv + 334. ill.

FOOD INDUSTRIES MANUAL. 12th edition. London 1942. pp. 321. ill.

FORBES, E. B., and KEITH, M. H. A review of the literature of phosphorus compounds in animal metabolism. (*Ohio Agric. Exper. Station, Tech. Ser., Bull. No.* 5). Wooster 1914. pp. 748.

FREY, M.v. *See* WOOLDRIDGE, L. C.

FROMM, EMIL. Die chemischen Schutzmittel des Tierkörpers bei Vergiftungen. Strassburg 1903. pp. 32.

GAYDON, A. G. Spectroscopy and combustion theory. London 1942. pp. x + 191. ill.

GIBB, T. R. P. Optical methods of chemical analysis. New York 1942. pp. xiv + 391. ill.

GIRAL, FRANCISCO. *See* ROJAHN, C. A.

GLASSTONE, SAMUEL. *See* TAYLOR, H. S.

GRANT, JULIUS. Science for the prosecution. London 1941. pp. viii + 302. ill.

—— A laboratory handbook of pulp and paper manufacture. Incorporating the 4th edition of Stevens's "Paper mill chemist." London 1942. pp. viii + 320. ill.

GREGORY, T. C. *See* CONDENSED CHEMICAL DICTIONARY.

GUICHARD, P. Précis de chimie industrielle. Paris 1894. pp. viii + 422. ill.

HARPER, H. *See* BRUCE, J.

HARTWELL, J. L. *See* UNITED STATES PUBLIC HEALTH SERVICE. *National Cancer Institute.*

HATFIELD, W. H. *See* INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

HEALEY, R. H., and REED, J. W. The behaviour of slow electrons in gases: an account of diffusion methods together with a comparison between results obtained by these and by various other methods. Sydney 1941. pp. xii + 179. ill.

HENDERSON, WILLIAM. *See* CLAPPERTON, ROBERT HENDERSON.

HÉRISSEY, H. Recherches chimiques et physiologiques sur la digestion des mannanes et des galactanes, par la séminase chez les végétaux. Lille 1903. pp. 87.

HIGGINS, A. E. H. *See* DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

HIGH POLYMERS. Vol. IV. Natural and synthetic high polymers. By K. H. MEYER. Translated by L. E. R. PICKEN. New York 1942. pp. xviii + 690. ill.

HIMUS, GODFREY W. Fuel testing. 2nd edition. London 1942. pp. xvi + 288.

HOARE, W. E. *See* TIN RESEARCH INSTITUTE. Publication No. 107.

HOFMEISTER, FRANZ. Die chemische Organisation der Zelle. Braunschweig 1901. pp. 29.

HOLDER, E. J. Surgical sutures and ligatures. Edinburgh 1939. pp. 64. ill.

HUDSON, O. F. *See* NIGHTINGALE, S. J.

HÜCKEL, W. Theoretische Grundlagen der organischen Chemie. 3rd edition. Vol. I. Leipzig 1940. pp. xii + 616. (*Reference.*)

INDIAN LAC RESEARCH INSTITUTE. Practical applications of recent lac research. Edited by H. K. SEN. Namkum 1940. pp. viii + 78 + vi. ill.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. "The precious metals." By H. GORDON DALE. 24th Streatfeild Memorial Lecture. London 1941. pp. 20. ill.

—— Lecture on rust-, acid- and heat-resisting steels. By W. H. HATFIELD. London 1942. pp. 48. ill.

INSTITUTE OF PETROLEUM. Annual Reviews of Petroleum Technology. Vol. VI. Birmingham 1941. pp. iv + 318. ill. (*Reference.*)

—— Standard methods for testing petroleum and its products. 4th edition. London 1942. pp. xvi + 390. ill.

INTER-SOCIETY COLOR COUNCIL. *See* AMERICAN SOCIETY FOR TESTING MATERIALS.

IODINE EDUCATIONAL BUREAU. Iodine facts. No. 1, etc. London 1940 +. (*Reference.*)

ISELY, DWIGHT. Methods of insect control. 2nd edition. 2 parts. Minneapolis 1941—42. pp. ii + 121, ii + 135.

JACOBS, M. B. War gases: their identification and decontamination. New York 1942. pp. xiv + 180. ill.

JOLLES, ADOLF. Die Fette vom physiologisch-chemischen Standpunkte. Strassburg 1907. pp. 71.

JOURNAL OF BIOCHEMISTRY. Vol. XXV. Tokyo 1937. (*Reference.*)

JOURNAL OF INDUSTRIAL HYGIENE AND TOXICOLOGY. Vol. XXII. Baltimore 1940.

KASTLE, J. H. The oxidases and other oxygen-catalysts concerned in biological oxidations. (*U.S. Hygienic Lab., Bull. No.* 59.) Washington 1910. pp. 164.

KAYE, G. W. C., and LABY, T. H. Tables of physical and chemical constants and some mathematical functions. 9th edition. London 1941. pp. viii + 181. (*Reference.*)

KEITH, M. H. *See* FORBES, E. B.

KISTLER, S. S. *See* ADVANCES IN COLLOID SCIENCE.

KLIMONT, J. *See* ULZER, F.

KLOOSTER, HENRY S. VAN. *See* DAVISON, ALBERT W.

KNAGGS, I. E., and KARLIK, B. Tables of cubic crystal structure of elements and compounds. With a section on alloys by C. F. ELAM. London 1932. pp. 90.

KOEBEL, N. K. Industrial controlled atmospheres. [2nd edition.] Chicago 1942. pp. xii + 97. ill.

KOLTHOFF, I. M., and LAITINEN, H. A. *p*H and electro titrations. 2nd edition. New York 1941. pp. x + 190. ill.

KOLTHOFF, I. M., and STENGER, V. A. Volumetric analysis. 2nd edition. Vol. I. New York 1942. pp. xvi + 309. ill.

KRAEMER, ELMER O. *See* ADVANCES IN COLLOID SCIENCE.

KRÄNZLEIN, GEORG. Aluminiumchlorid in der organischen Chemie. 3rd edition. Edited by P. KRÄNZLEIN. Berlin 1939. pp. 281.

KRÄNZLEIN, P. *See* KRÄNZLEIN, GEORG.

KROGH, A. The comparative physiology of respiratory mechanisms. Philadelphia 1941. pp. viii + 172. ill.

LABY, T. H. *See* KAYE, G. W. C.

LAITINEN, G. W. C. *See* KOLTHOFF, I. M.

LANFORD, CAROLINE SHERMAN. *See* SHERMAN, HENRY C.

LECOMTE, J. Le spectre infrarouge. Paris 1928. pp. 468. ill.

LEIGHTON, PHILIP ALBERT. *See* NOYES, WILLIAM ALBERT, jun.

LEWIS, HOWARD B. *See* BIOLOGICAL SYMPOSIA.

LEWIS, W. K., SQUIRES, L., and BROUGHTON, G. Industrial chemistry of colloidal and amorphous materials. New York 1942. pp. xiv + 540. ill.

LIEBIG, JUSTUS VON. Die organische Chemie in ihrer Anwendung auf Agrikultur und Physiologie. Braunschweig 1940. pp. xii + 352.

—— Gährung, über Quelle der Muskelkraft und Ernährung. Leipzig 1870. pp. xii + 138.

LOVERN, J. A. *See* DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. *Food Investigation.* Special Report No. 52.

MCALPINE, R. K., and SOULE, B. A. Fundamentals of qualitative chemical analysis. 2nd edition. New York 1941. pp. xii + 375.

MACORMAC, A. R. *See* MERRILL, G. R.

MANTELL, C. L. [and others]. The technology of natural resins. New York 1942. pp. viii + 506. ill.

MAQUENNE, L. Les sucres et leurs principaux dérivés. Paris 1900. pp. viii + 1032.

MARSH, J. T., and WOOD, F. C. An introduction to the chemistry of cellulose. 2nd edition. London 1942. pp. xvi + 512. ill.

MARTINDALE, [W. H.]. The extra pharmacopœia. 22nd edition. Vol. I. London 1941. pp. xl + 1289. (*Reference.*)

MATHEWS, J. HOWARD. *See* DANIELS, FARRINGTON.

MATTICE, M. R. *See* BRIDGES, M. A.

MATTIELLO, JOSEPH J. [Editor.] Protective and decorative coatings: paints, varnishes, lacquers and inks. Vol. I. Raw materials for varnishes and vehicles. New York 1941. pp. xii + 819. ill.

MAUERSBERGER, H. R. *See* MERRILL, G. R.

MAXFIELD, FREDERICK A., and BENEDICT, R. RALPH. Theory of gaseous conduction and electronics. New York 1941. pp. xiv + 483. ill.

MAZÉ, P. Évolution du carbone et de l'azote dans le monde vivant. Paris 1899. pp. 110.

MEES, C. E. K. The theory of the photographic process. New York 1942. pp. x + 1124. ill.

MERCK & Co. The Merck manual of therapeutics and materia medica. 7th edition. Rahway 1940. pp. x + 1436. (*Reference.*)

MERRILL, G. R., MACORMAC, A. R., and MAUERSBERGER, H. R. American cotton handbook: a practical reference book for the entire cotton industry. New York 1941. pp. [xx] + 1024. ill. (*Reference.*)

MERZ, A. Bewertung chemisch gefällter Kreiden nach neuzeitlichen Gesichtspunkten. Dresden 1939. pp. viii + 49. ill.

MEYER, K. H. *See* HIGH POLYMERS.

MEYERHOF, O. [and others]. A symposium on respiratory enzymes. Madison 1942. pp. xii + 281. ill.

MIESCHER, FRIEDRICH. Die histochemischen und physiologischen Arbeiten. 2 vols. Leipzig 1897. pp. iv + 138, vi + 543. ill.

MINISTRY OF AGRICULTURE AND FISHERIES. Bulletin No. 124. The composition and nutritive value of feeding stuffs. By H. E. WOODMAN. London 1942. pp. 22.

MOHR, L., and BEUTTENMÜLLER, H. Die Methodik der Stoffwechseluntersuchungen. Wiesbaden 1911. pp. x + 176. ill.

MOREL, ALBERT. Précis de technique chimique à l'usage des laboratoires médicaux. Paris 1909. pp. iv + 832. ill.

MORTON, AVERY ADRIAN. Laboratory technique in organic chemistry. New York 1938. pp. x + 261. ill.

MORTON, R. A. The application of absorption spectra to the study of vitamins, hormones and coenzymes. 2nd edition. London 1942. pp. 226. ill.

MOULTON, FOREST RAY. *See* AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

NATIONAL FEDERATION OF GAS COKE ASSOCIATIONS, BRITISH HARD COKE ASSOCIATION and SOUTH WALES ANTHRACITE AND DRY COAL COMMITTEE. Producer gas plant for industrial purposes: its operation and maintenance. London 1942. pp. viii + 88. ill.

NEEDHAM, J. Biochemistry and morphogenesis. Cambridge 1942. pp. xvi + 787. ill.

NELSON, W. L. Petroleum refinery engineering. 2nd edition. New York 1941. pp. x + 715. ill.

NICHOLLS, J. R. Aids to the analysis of foods and drugs. 6th edition. London 1942. pp. viii + 424.

NIEDERL, J. B., and NIEDERL, V. Micromethods of quantitative organic analysis. 2nd edition. New York 1942. pp. xiv + 347. ill.

NIEDERL, V. *See* NIEDERL, J. B.

NIGHTINGALE, S. J. Tin solders. 2nd edition. Revised by O. F. HUDSON. London 1942. pp. xii + 117. ill.

NOYES, WILLIAM ALBERT, jun., and LEIGHTON, PHILIP ALBERT. The photochemistry of gases. (American Chemical Society, Monograph Series.) New York 1941. pp. 475. ill.

ORGANIC SYNTHESES. Collective Vol. I. 2nd edition. New York 1941. pp. xii + 580. ill. (*Reference.*)

OSBORNE, THOMAS B. The proteins of the wheat kernel. Washington 1907. pp. 119.

OSWALD, ADOLPH. Ueber die chemische Beschaffenheit und die Function der Schilddrüse. Strassburg 1900. pp. 61.

PALMER, W. G. Experimental physical chemistry. Cambridge 1941. pp. xii + 321. ill.

PATERSON, THOMAS STEWART. *See* ALCHEMIST, THE.

PAULI, WOLFGANG. Der kolloidale Zustand und die Vorgänge in der lebendigen Substanz. (From the *Naturwiss. Rundschau*, 1902, 17.) pp. 32.

PEARSON, C. S. *See* SHERMAN, H. C.

PERRY, JOHN H. *See* CHEMICAL ENGINEERS' HANDBOOK.

PFLÜCKE, M. *See* DEUTSCHE CHEMISCHE GESELLSCHAFT.

PICKEN, L. E. R. *See* HIGH POLYMERS.

PIETTRE, M. Recherches sur la bile. Laval 1910. pp. xii + 225. ill.

PIGOTT, E. C. The chemical analysis of ferrous alloys and foundry materials. London 1942. pp. xvi + 362.

"PLASTES." Plastics in industry. 2nd edition. London 1942. pp. xiv + 248. ill.

PLUMMER, H. *See* TIN RESEARCH INSTITUTE. Publication No. 107.

RATHERY, F. *See* BIERRY, H.

READ, J. Explosives. London 1942. pp. 160. ill.

REED, J. W. *See* HEALEY, R. H.

REMINGTON, J. S. The paint laboratory note book. 2nd edition. London 1942. pp. xii + 138. ill.

RHODES, THOMAS J. Industrial instruments for measurement and control. New York 1941. pp. x + 573. ill.

RICHTER, V. VON. Organic chemistry. 3 vols. London 1915—23. (*For circulation.*)

ROBINSON, G. W. Soils: their origin, constitution, and classification. London 1932. pp. xvi + 390. ill.

ROJAHN, C. A. Preparación de productos quimicos y quimico-farmaceuticos. Translated from the German and amplified by F. GIRAL. 2 vols. Mexico 1942. pp. xl + 458, 459 to 1002.

ROSENBERG, H. R. Chemistry and physiology of the vitamins. New York 1942. pp. xx + 674. ill.

RUHEMANN, B. *See* RUHEMANN, M.

RUHEMANN, M., and RUHEMANN, B. Low temperature physics. Cambridge 1937. pp. x + 313. ill.

SALKOWSKI, ERNST. *See* BEITRÄGE ZUR WISSENSCHAFTLICHEN MEDICIN UND CHEMIE.

SCHADE, H. Die physikalische Chemie in der inneren Medizin. Dresden 1921. pp. viii + 569. ill.

SCHITTENHELM, ALFRED. *See* BRUGSCH, THEODOR.

SCHOLES, SAMUEL R. Modern glass practice. [Revised edition.] Chicago 1941. pp. vi + 289. ill.

SCHURECHT, H. G., and WOOD, K. T. The use of borax and boric acid together with salt in salt glazing. New York 1942. pp. 48. ill.

SCOFFERN, J. A manual of chemical analysis for the young. London [1854]. (*Reference.*)

SEIFRIZ, W. *See* AMERICAN SOCIETY OF PLANT PHYSIOLOGISTS.

SHERMAN, HENRY C. Chemistry of food and nutrition. 6th edition. New York 1941. pp. xii + 611. ill.

SHERMAN, HENRY C., and LANFORD, CAROLINE SHERMAN. Essentials of nutrition. New York 1940. pp. x + 418. ill.

SHERMAN, HENRY C., and PEARSON, C. S. Modern bread from the viewpoint of nutrition. New York 1942. pp. x + 118.

SHIMIZU, T. Über die Chemie und Physiologie der Gallensäuren. Okayama 1935. pp. xviii + 388. ill.

SIMONDS, H. R. Industrial plastics. [2nd edition.] New York 1941. pp. xii + 385. ill.

SOULE, BYRON A. Library guide for the chemist. New York 1938. pp. xiv + 302.

— *See* MCALPINE, R. K.

SOUTH WALES ANTHRACITE AND DRY COAL COMMITTEE. *See* NATIONAL FEDERATION OF GAS COKE ASSOCIATIONS.

SQUIRES, L. *See* LEWIS, W. K.

STEINER, LUKE E. Introduction to chemical thermodynamics. New York 1941. pp. xiv + 516. ill.

STENGER, V. A. *See* KOLTHOFF, I. M.

STRAIN, HAROLD H. Chromatographic adsorption analysis. New York 1942. pp. x + 222. ill.

SUTERMEISTER, EDWIN. Chemistry of pulp and paper making. 3rd edition. New York 1941. pp. xii + 529. ill.

TAYLOR, H. S., and GLASSTONE, SAMUEL. [Editors.] A treatise on physical chemistry. 3rd edition. Vol. I. New York 1942. pp. viii + 679. ill.

TEXAS COMPANY, THE. Physical constants of the principal hydrocarbons. 3rd edition. Compiled by M. P. Doss. New York 1942. pp. x + 215.

THATCHER, ROSCOE W. The chemistry of plant life. New York 1921. pp. xvi + 268.

THOMAS, C. A., [and others]. Anhydrous aluminum chloride in organic chemistry. (American Chemical Society, Monograph Series.) New York 1942. pp xiv + 972. ill.

THOMAS, P. Recherches biochimiques sur les protéiqes de la levure. Laval 1919. pp. vi + 166.

THUDICHUM, J. L. W. Die chemische Konstitution des Gehirns des Menschen und der Tiere. Tübingen 1901. pp. xii + 339.

— *See* ANNALS OF CHEMICAL MEDICINE.

TIN RESEARCH INSTITUTE. Publication No. 107. Hot-tinning "difficult" mild steels. By W. E. HOARE and H. PLUMMER. Greenford 1941. pp. 28. ill.

TITANIUM ALLOY MANUFACTURING CO. Titanium and its use in steel. New York 1940. pp. 113. ill.

ULZER, F., and KLIMONT, J. Allgemeine und physiologische Chemie der Fette. Berlin 1906. pp. xii + 317. ill.

UNITED STATES PUBLIC HEALTH SERVICE. *National Cancer Institute.* Survey of compounds which have been tested for carcinogenic activity. By J. L. HARTWELL. [Washington] 1941. pp. 371. (*Reference.*)

VERNON, H. M. Intracellular enzymes. London 1908. pp. xii + 240.

VILBRANDT, F. C. Chemical engineering plant design. 2nd edition. New York 1942. pp. x + 452. ill.

WAISMAN, HARRY A., and ELVEHJEM, C. A. The vitamin content of meat. Minneapolis 1941. pp. iv + 210. (Two copies.)

WELCHER, FRANK. Chemical solutions: reagents useful to the chemist, biologist, and bacteriologist. New York 1942. pp. viii + 404. (*Reference.*)

WHITTAKER, C. M., and WILCOCK, C. C. Dyeing with coal-tar dyestuffs. 4th edition. London 1942. pp. viii + 371. ill.

WILCOCK, C. C. *See* WHITTAKER, C. M.

WILLIAMS, HAL. Mechanical refrigeration. 5th edition. London 1941. pp. xii + 564. ill.

WILLIAMS, JOHN WARREN. *See* DANIELS, FARRINGTON.

WILLIAMS, S. R. Hardness and hardness measurements. Cleveland 1942. pp. viii + 558. ill.

WILSON, J. S. The pasteurization of milk. London 1942. pp. xii + 212. ill.

WOOD, F. C. *See* MARSH, J. T.

WOODMAN, H. E. *See* MINISTRY OF AGRICULTURE AND FISHERIES. Bulletin No. 124.

WOODROFFE, D. Fundamentals of leather science. Croydon 1941. pp. 158. ill.

WOOLDRIDGE, L. C. Die Gerinnung des Blutes. Edited by M. v. FREY. Leipzig 1891. pp. xii + 51.

WOOLDRIDGE, W. R. War gases and foodstuffs: chemical warfare and food supplies. London 1942. pp. iv + 50. ill.

WURTZ, A. La théorie atomique. 8th edition. Paris 1898. pp. lvi + 248. ill.

ZERBAN, F. W. *See* BROWNE, C. A.

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD., BUNGAY, SUFFOLK.

PUBLICATIONS OF THE SOCIETY

With the exception of certain publications which are out of print, the following may be obtained from the General Secretary:

		Price to Fellows. £	s.	d.	Price to Public. £	s.	d.
Memoirs and Proceedings, 1841–1847 (3 vols.)	per vol.	2	10	0	3	5	0
Quarterly Journal, 1848–1861 (14 vols.)	per vol.	2	10	0	3	5	0
" " " "	per part		5	0		6	6
Journal, 1862–1870	per vol.	2	10	0	3	5	0
" (including Abstracts), 1871–1923	per part		5	0		6	6
* " 1924–1940	per vol.	2	15	0	3	10	0
* " 1941–1942	per part		5	6		7	6
†British Chemical Abstracts "A" (Pure Chemistry), 1924–1937	per vol.	2	10	0	3	15	0
	per part		5	0		7	6
†British Chemical Abstracts Annual Index, 1926–1937	per copy		5	0		11	0
†British Chemical and Physiological Abstracts "A," 1938–1940:							
A. I (General, Physical and Inorganic Chemistry)	per ann.		17	6	2	5	0
A. II (Organic Chemistry)	per ann.		17	6	2	5	0
A. III (Physiology and Biochemistry)	per ann.	1	7	6	3	5	0
1941–1942							
A. I (General, Physical and Inorganic Chemistry)	per ann.	1	0	0	2	10	0
A. II (Organic Chemistry)	per ann.	1	0	0	2	10	0
A. III (Physiology and Biochemistry)	per ann.	1	12	0	4	0	0
(Including one copy of the Index in each case.)							
(Prices of combinations of above to public obtainable on application.)							
†Index to British Chemical and Physiological Abstracts, 1938, including "A" (Pure Chemistry and Physiology) and "B" (Applied Chemistry)			10	0		15	0
1939 (A only)			7	6		11	0
1940, 1941 and 1942 (A only)			6	0		8	6
‡Proceedings, 1885–1914	per vol.		7	6		7	6§
" "	per part			6			6§
Annual Reports on the Progress of Chemistry:							
Vol. I (1904)—Vol. XX (1923)	per copy		6	0		7	6§
Vol. XXI (1924)—Vol. XXXIII (1936)	per copy		8	6		10	6§
Vols. XXXIV—XXXVI (1937–1939)	per copy		8	6		13	0
Vol. XXXVII (1940)—	per copy		8	6		15	0
Collective Index, Vol. I, 1841–1872	per vol.		2	0§		2	0§
" " " II, 1873–1882	per vol.		5	0§		5	0§
" " " III, 1883–1892	per vol.		7	6§		7	6§
" " " IV, 1893–1902	per vol.		10	0§		10	0§
" " " V, 1903–1912	per vol.	2	0	0§	2	10	0§
" " " VI, 1913–1922	per vol.	3	5	0§	5	0	0§
†Decennial Index of British Chemical Abstracts, 1923–1932		4	0	0§	8	0	0
†Quinquennial Index of British Chemical Abstracts, 1933–1937		4	0	0§	10	0	0
(Obtainable from the Bureau of Chemical and Physiological Abstracts, Clifton House, Euston Road, N.W.1.							
Jubilee Volume (giving history of the Chemical Society from 1841 to 1891)			2	6		2	6§
Memorial Lectures, Vol. I, 1893–1900 (Reproduced)			9	0		10	6§
" " " II, 1901–1913 "			7	0		8	0§
" " " III, 1914–1932			5	0		6	0§
Volume of Faraday Lectures			5	6		8	6§
Portraits of Eminent Chemists, set of 8			18	0	1	2	0§
" " " each			2	6		3	0§
Tables of International Atomic Weights for 1942 (as recommended by the Committee on Atomic Weights of the Union Internationale de Chimie)	On cards: per doz.		1	6		2	0§
	per 50		5	6		7	6§
	per 100		10	6		14	0§

* *As from January, 1924, the Abstracts were separated from the Transactions and were published independently.* † *Issued by the Bureau of Chemical and Physiological Abstracts.*
‡ *Included with Journal as from January, 1915.* § *Postage extra. All other publications post free.*

NOTICES TO AUTHORS OF PAPERS

1. All Scientific Communications for the Journal should be addressed to "The Secretaries, Chemical Society, Burlington House, W.1." Papers to be read before a meeting of the Society are selected by the Secretaries.

2. A paper is not normally considered for publication in the Journal unless at least one of the authors is a Fellow of the Society, but in exceptional circumstances the Council is prepared to consider papers submitted by non-Fellows.

3. An author must submit with every paper a signed form of declaration that to the best of his knowledge the paper does not contain any information that contravenes the Official Secrets Act.

4. An author engaged in any Government Department or similar body associated with the prosecution of the war must submit with his paper a written declaration from such Department or body that he has received authority to submit the paper for consideration for publication in the Journal.

5. All papers should be submitted in typescript in double-line spacing. Footnotes in papers add considerably to the cost of printing; authors are requested, therefore, not to use them unless necessary.

6. Every paper should be prefaced by a short summary setting forth briefly and in simple language the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. The summary should be such as to enable any chemist to obtain a clear idea of what the investigation has achieved and should normally be from 50—250 words in length.

7. If he desires to do so, an author may send with the paper, for consideration by the Publication Committee, a confidential report by a Chemist of standing to whom the paper has been submitted.

8. The Publication Committee invites authors who publish series of related papers in the Journal to submit, at suitable intervals, papers reviewing their previously published work (suspended during the war).

9. The Society reserves the right to retain the Manuscript and illustrative drawings of all papers sent to it, and authors are therefore advised to keep copies. This right is not usually exercised in respect of illustrative drawings. When papers have been accepted for publication the authors are not at liberty, save by permission of the Council, to publish them elsewhere until such papers have appeared in the Journal of the Society. Papers which are retained by the Council after being judged unsuitable for publication in the Journal are deposited in the Archives of the Society.

10. Communications which have appeared in any other Journal shall not be published in the Journal of the Chemical Society unless this course is approved by a special vote of the Council.

11. The address to which proofs are to be sent should be written on every paper.

12. Authors resident overseas are requested to name agents in Britain to whom may be referred matters concerning their papers, including the correction of proofs, in order that delay in publication may be avoided.

13. Illustrations accompanying the papers must be carefully drawn, preferably **twice** the size of the finished block (max. width, 4½ inches), **in Indian ink,** on **smooth white Bristol board or paper.** Any illustration which exceeds four times the size of the finished block will be returned to the author for re-drawing to a smaller scale. Lettering on the drawings, whether on the margin or in the body of the drawing, must not be in ink but must be inserted *lightly in blue pencil.* Authors may, if they wish, submit in the first place clearly drawn pencil sketches instead of the completed diagrams, which, however, must be supplied before publication. Further information can be obtained from Dr. C. Smith, Staplefield Grange Farm, Haywards Heath, Sussex.

14. If any Author requires more than the number of reprints (without wrappers) allowed by the Society, namely, 10 plus 10 extra for each author in excess of one, or desires to receive his reprints in wrappers and is willing to pay the extra cost thereby involved, he should inform Dr. Smith at the time he sends in the corrected proof. Extra copies will be supplied at rates which can be obtained from the Editor.